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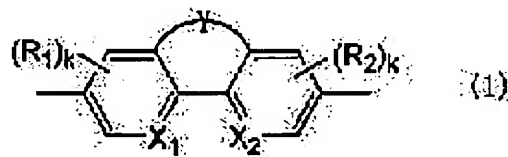
SAI HEIKI

(54) POLYMER COMPOUND AND PRODUCING METHOD AND USING METHOD THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a novel electron accepting polymer compound; and a method for producing and a method for using the same.

SOLUTION: The polymer compound comprises having a structure represented by formula (1) in the principal chain, wherein X1 and X2 are same or different each other and carbon constituting the benzene ring or nitrogen constituting the pyridine ring; R1 and R2 are same or different each other and a substituent group; k is 0, 1, 2 or 3 if X1 and X2 constitute benzene rings and is 0, 1 or 2 if X1 and X2 constitute pyridine rings; Y is an atom or an atomic group necessary to complete a 5-7 membered heterocycle.



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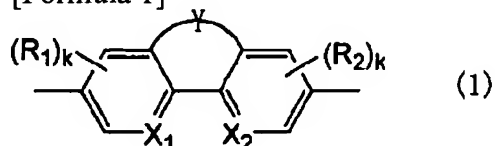
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CLAIMS

[Claim(s)]

[Claim 1] The high molecular compound which has the structure shown by the following formula (1) in a principal chain.

[Formula 1]



In [type (1), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member.]

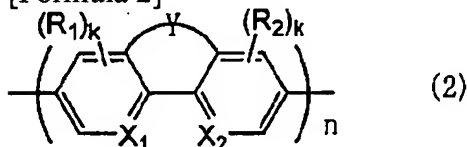
[Claim 2] The high molecular compound of claim 1 whose X1 and X2 in a formula (1) are nitrogen which constitutes a pyridine ring.

[Claim 3] The high molecular compound of claims 1 or 2 whose Y in a formula (1) is O, S, N=N, or R11 N-CO-NR12 (however, R11 and R12 may be the same respectively, or may differ from each other, and express hydrogen or a substituent.).

[Claim 4] One high molecular compound of claims 1-3 whose molecular weight is 1000 or more in weight average molecular weight.

[Claim 5] One high molecular compound of claims 1-4 shown by the formula (2).

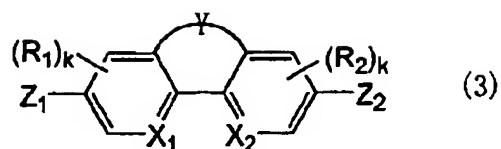
[Formula 2]



In [type (2), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. n expresses polymerization degree and is 5-1000.]

[Claim 6] The manufacture approach of the high molecular compound obtained by carrying out dehalogenation of the dihalogen compound shown by the following formula (3) in one high molecular compound of claims 1-5, and carrying out a polymerization.

[Formula 3]

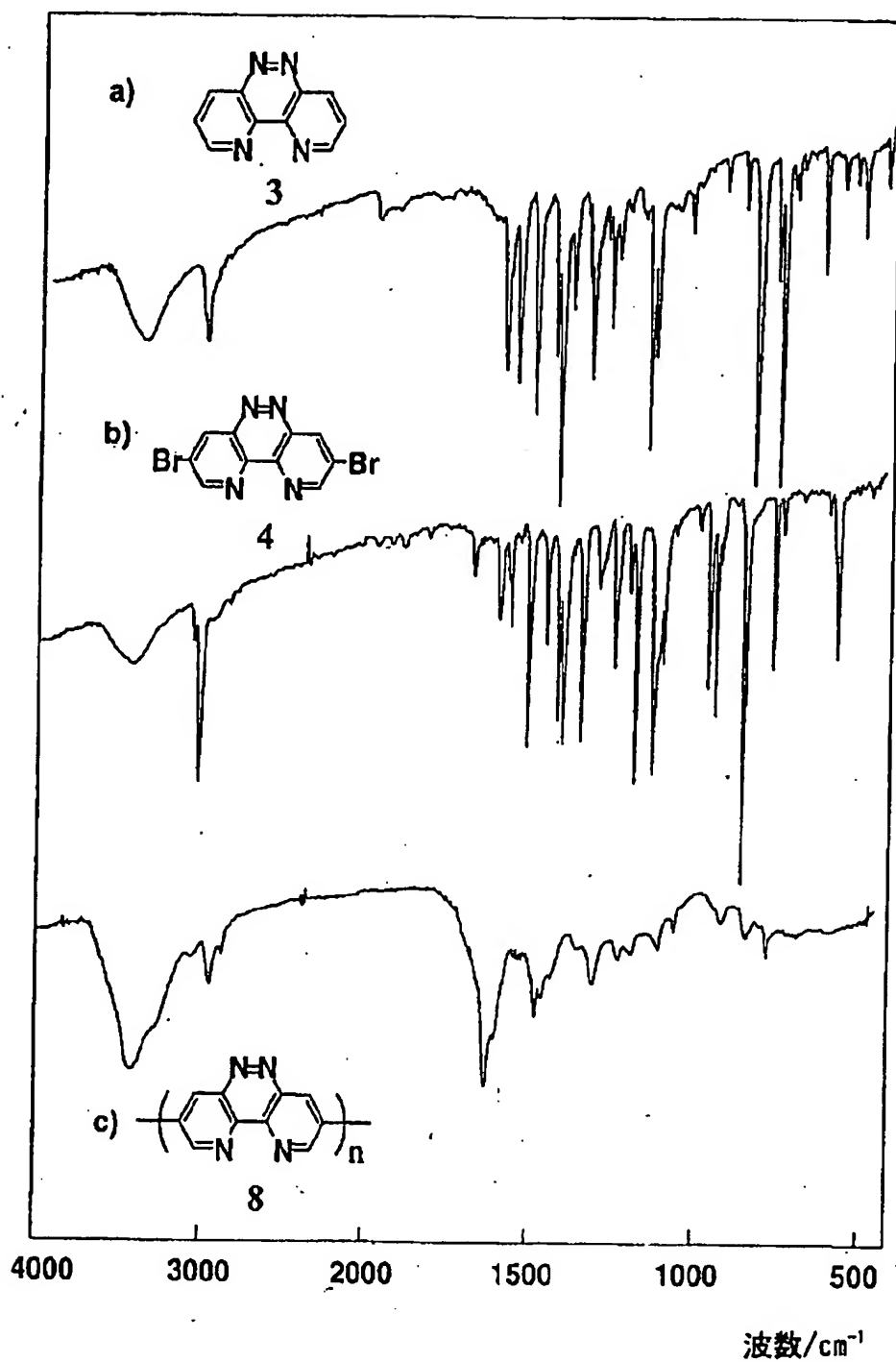



In [type (3), X_1 and X_2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R_1 and R_2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X_1 and X_2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. Z_1 and Z_2 may be the same respectively, or they may differ from each other, and express a halogen.]

[Claim 7] The manufacture approach of the high molecular compound of claim 6 that a dehalogenation polymerization is performed under existence of copper or a zero ** nickel compound.

[Claim 8] The usage of the high molecular compound which uses one high molecular compound of claims 1-5 as electrochromic materials or an active material for cells.

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Drawing selection drawing 1 

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new high molecular compound which has pi conjugated system which met the principal chain, the high molecular compound which can specifically expect the application as an ingredient for functional organic devices, such as an organic electroluminescence device and an organic FET (field-effect transistor) device, about the manufacture approach, and its manufacture approach. Moreover, it is related with the usage as electrochromic materials and an active material for cells.

[0002]

[Description of the Prior Art] In recent years, pi conjugation high molecular compound attracts attention as an electric and optical functional material, for example, is applied to the rechargeable battery, an organic electroluminescence device or an organic FET device, etc. For example, poly para-phenylene vinylene (PPV), poly para-phenylene (PPP), etc. are used for an organic electroluminescence device, and the poly aniline, the poly thiophene, etc. are used for the organic FET device for the poly thiophene etc. at the rechargeable battery. However, since many of ingredients developed so far are electron-donative giant molecules, the constraint of ** to which the design of a device is restricted has arisen. For example, it is a device deficient in the electronic transport capacity which most devices by which the current report is carried out become from an electron-donative ingredient in the field of a giant-molecule EL device, and an improvement of the further property is possible by combining with the polymeric materials from which it has electronic receptiveness and the property as an n mold conductor is expected. Moreover, although many reports of the p mold FET device of the electron-donative poly thiophene base are carried out in the field of the FET device using a conductive polymer, the FET device using an electronic receptiveness giant molecule is not yet reported, but an appearance of the polymeric materials which show n mold property with electronic receptiveness is desired.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer [new pi conjugation high molecular compound which can expect the application as a functional material of functional organic devices, such as an organic electroluminescence device and an organic FET device, and which has electronic receptiveness, and] the manufacture approach. Moreover, it is offering the usage as electrochromic materials and an active material for cells.

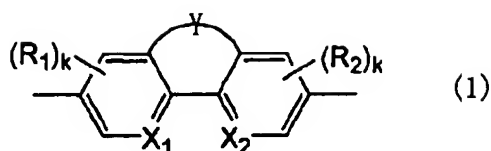
[0004]

[Means for Solving the Problem] Such a purpose is attained by following this invention.

[0005] (1) The high molecular compound which has the structure shown by the following formula (1) in a principal chain.

[0006]

[Formula 4]



[0007] In [type (1), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member.]

(2) The high molecular compound of the above (1) whose X1 and X2 in a formula (1) are nitrogen which constitutes a pyridine ring.

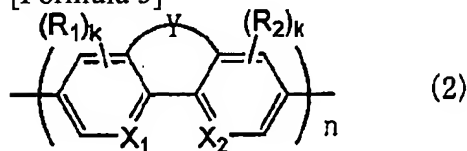
(3) The above (1) whose Y in a formula (1) is O, S, N=N, or R11 N-CO-NR12 (however, R11 and R12 may be the same respectively, or may differ from each other, and express hydrogen or a substituent.), or (2) high molecular compounds.

(4) One high molecular compound of above-mentioned (1) - (3) whose molecular weight is 1000 or more in weight average molecular weight.

(5) One high molecular compound of above-mentioned (1) - (4) shown by the formula (2).

[0008]

[Formula 5]

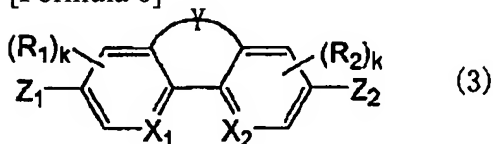


[0009] In [type (2), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. n expresses polymerization degree and is 5-1000.]

(6) The above (1) The manufacture approach of the high molecular compound obtained by carrying out dehalogenation of the dihalogen compound shown by the following formula (3) in one high molecular compound of - (5), and carrying out a polymerization.

[0010]

[Formula 6]



[0011] In [type (3), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. Z1 and Z2 may be the same respectively, or they may differ from each other, and express a halogen.]

(7) The manufacture approach of the high molecular compound the above (6) that a dehalogenation polymerization is performed under existence of copper or a zero ** nickel compound.

(8) The above (1) Usage of the high molecular compound which uses one high molecular compound of - (5) as electrochromic materials or an active material for cells.

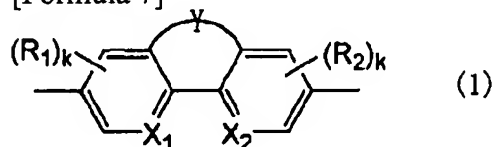
[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0013] The high molecular compound of this invention is a high molecular compound which has the structure shown by the following formula (1) in a principal chain, and is new pi conjugation high molecular compound which has electronic receptiveness.

[0014]

[Formula 7]



[0015] In a formula (1), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member.

[0016] When it explains further, X1 and X2 are the same, and when making electronic receptiveness discover, the combination of nitrogen is usually desirable [two] about a formula (1).

[0017] The substituents expressed with R1 and R2 may be any, for example, a nitro group, the amino group, etc. may be desirable and may be an alkyl group of carbon numbers 1-3 etc. As for k, it is desirable that it is 0 (namely, thing which does not have a substituent other than predetermined association) in any [of the benzene ring and a pyridine ring] case.

[0018] As the atom or the atomic group expressed with Y, preferably, O, S, N=N, R11 N-CO-NR12, etc. are mentioned, and O, N=N, R11 N-CO-NR12, etc. are desirable especially. Here, they may be the same respectively, or may differ and express hydrogen or a substituent (for example, alkyl group of carbon numbers 1-3), the usually same thing of R11 and R12 is desirable, and its combination of hydrogen is especially desirable.

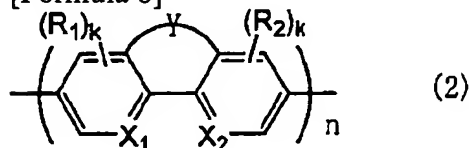
[0019] If the high molecular compound of this invention has the structure shown by the formula (1) in a principal chain, within limits which especially a limit does not have in the structure and do not check electronic receptiveness besides the configuration repeat unit of a formula (1) Although it has other configuration repeat units (for example, thing guided from a pyridine, a pyrimidine, a quinoline, a NAFUCHI lysine, etc.), it is desirable that it is the high molecular compound which consists of structure especially shown by the formula (1). In this case, although the configuration repeat unit of a formula (1) may be the same homopolymer and you may be the copolymer of the combination from which the configuration repeat unit of a formula (1) differs, it is desirable on a composite ease or a property that it is a homopolymer.

[0020] It is weight average molecular weight, as for the molecular weight of the high molecular compound of this invention, 1000 or more are desirable, and it is desirable to a pan that it is 3000-50000. It becomes easy to cast by having such molecular weight, and the reinforcement of mold goods improves by it.

[0021] As for especially the high molecular compound of this invention, what is shown by the following formula (2) is desirable, and its homopolymer is desirable especially.

[0022]

[Formula 8]

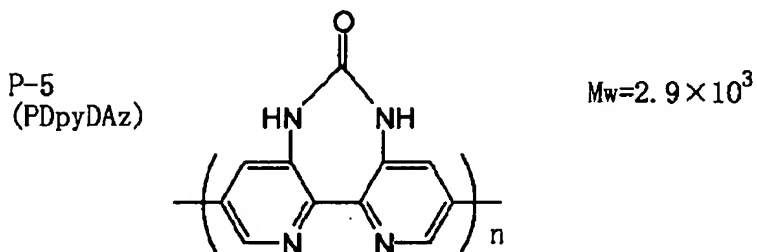
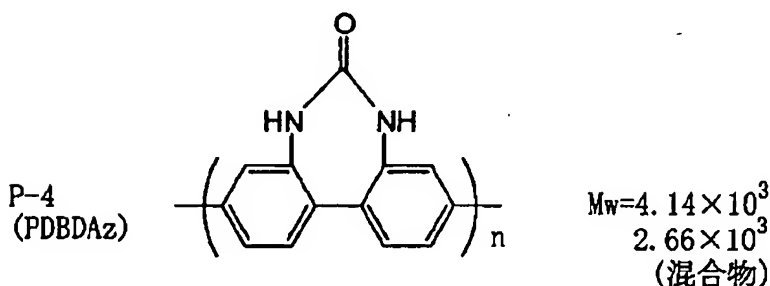
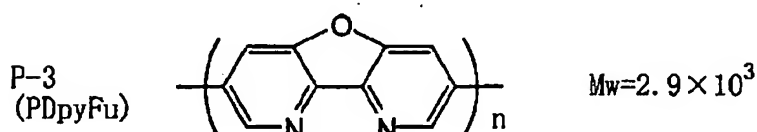
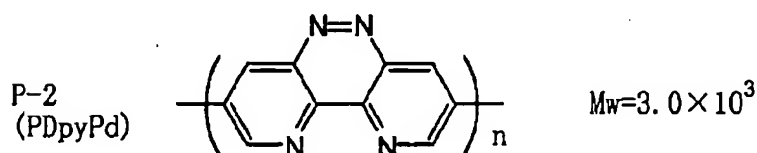
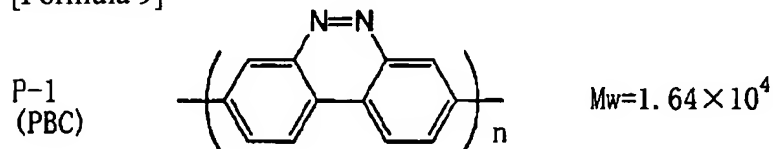


[0023] In a formula (2), X1, X2, R1, R2, k, and Y are a thing in a formula (1), and the thing of homonymy, and its same is said of a desirable thing. n is polymerization degree and is 5-1000.

[0024] Although the suitable example of the high molecular compound of this invention is shown below, it is not limited to these. It combines and weight average molecular weight Mw is shown. Moreover, all end groups are H.

[0025]

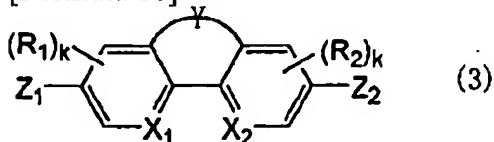
[Formula 9]



[0026] Such a high molecular compound is obtained by carrying out a polymerization while using as a start raw material the dihalogen compound shown by the following formula (3) according to the structure made into the purpose and carrying out dehalogenation of these.

[0027]

[Formula 10]



[0028] In a formula (3), X1, X2, R1, R2, k, and Y are a thing in a formula (1), and the thing of homonymy. Z1 and Z2 may be the same respectively, or they may differ from each other, and express a

halogen. Cl, Br, I, etc. are mentioned as a halogen expressed with Z1 and Z2. The same thing of Z1 and Z2 is desirable, and its combination of Br(s) etc. is desirable.

[0029] The metal or metallic compounds which has dehalogenation ability is made to exist on the occasion of dehalogenation and a polymerization. Various things are mentioned as the metal used for this invention, or metallic compounds. First, as a metal, the metal which causes the C-C coupling reaction of a reducibility metal or an organic halogenide is desirable, for example, 14 group metals, such as 13 group metals, such as 12 group metals, such as transition metals, such as 2 group metals, such as 1 group metals, such as Li, Na, and K, and Mg, calcium, and Ti, V, Cr, Fe, Co, nickel, Cu, and Zn, and aluminum, Ga, and Sn, are mentioned. the catalyst which consists of other metals or metallic compounds may be used for these metals if needed (the example which makes a nickel compound a catalyst in the similar polymerization using Mg -- a magazine "a macromolecule" -- indicated by the formula (1) in the 46th volume and 68 pages (1997)). Moreover, as metallic compounds, although there is especially no limit, the thing which makes the C-C coupling reaction of reducibility metallic compounds or an organic halogenide cause is desirable, for example, a zero ** nickel compound, a zero ** palladium compound, etc. are mentioned. When using these zero *****, such zero ***** itself may be used, and a divalent nickel compound, a divalent palladium compound, etc. may be added, and you may make it generate using reducing agents, such as Zinc Zn and a hydrazine, in the system of reaction. As a format of homopolymerization accompanied by C-C joint generation, polymerization formation of a publication can be mentioned [Japanese Patent Application No. / No. 42428 / six to] using a zero ** nickel compound.

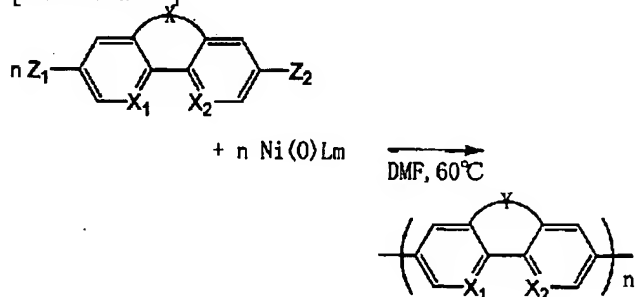
[0030] Copper or a zero ** nickel compound is desirable, and use of a zero ** nickel complex (for example, screw (1, 5-cyclo-octadiene) nickel:nickel2 (cod)) is desirable especially also in such.

[0031] Moreover, what is necessary is just to perform such a reaction at the temperature of about 60 degrees C using organic solvents, such as dimethylformamide (DMF), etc.

[0032] The reaction scheme in the case of obtaining the high molecular compound (however, k= 0) of a formula (2) is shown below.

[0033]

[Formula 11]



Ni(0)Lm : 0価ニッケル錯体
(Ni(cod)₂と2,2'-ビピリジルとの混合物)

[0034] Thus, the high molecular compound obtained can be identified with elemental analysis, an infrared absorption spectrum (IR), etc. moreover, molecular weight -- a gel permeation chromatograph (GPC) -- it asks by law.

[0035] The high molecular compound of this invention is an electronic receptiveness compound, and the application with electronic receptiveness, such as an organic electroluminescence device and an organic FET device, as polymeric materials is expected. Moreover, the thing of X1=X2=N can also expect the application as a macromolecule chelating agent to a metal among the high molecular compounds of this invention.

[0036] Moreover, since the electrochemical reduction reaction accompanied by change of a color is shown, the high molecular compound of this invention can be used as electrochromic materials.

Moreover, it can also be used as an active material for cells using a oxidation reduction function. About

these concrete application approaches and gestalten, it applies to a well-known thing correspondingly.
[0037]

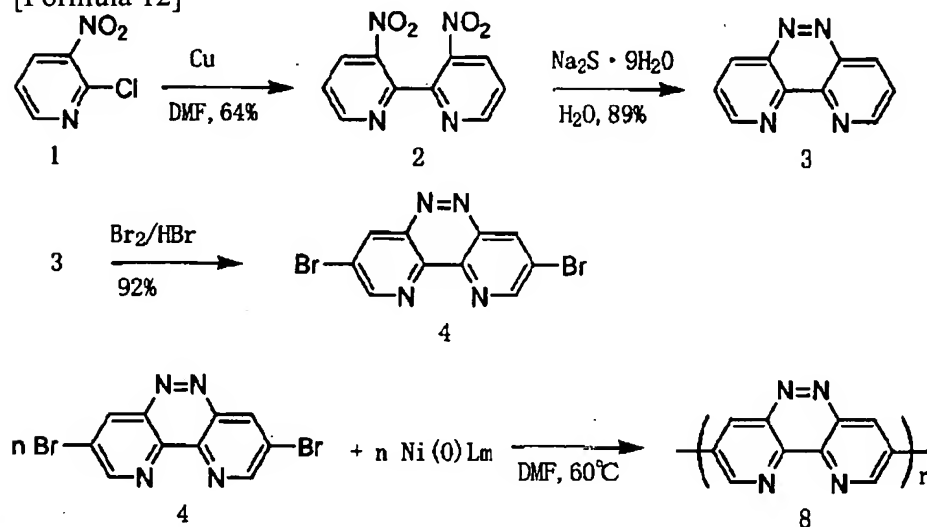
[Example] Hereafter, an example explains this invention concretely.

Example 1 (composition)

The reaction scheme of the synthetic high polymer P-2 of a high molecular compound P-2 (Pori (the JIPIRIDO [3, 2-c:2', 3'-e] pyridazine -3, 8-diyl)) is shown below.

[0038]

[Formula 12]



[0039] 1) Synthetic 1-13 of a monomer, 3-dinitro -2, a 2'-bipyridyl (2)

A 2-chloro-3-nitropyridine (1), (10g, 63.1mmol), N,N-dimethylformamide (30cm³), and the end (12g) of copper bronze powder were agitated all over the oil bath at 100 degrees C for 2 hours. The reaction mixture was filtered and aqueous ammonia was added to the filtration object. Precipitate was carried out the ** exception and the silica gel column chromatography refined it (eluent CHCl_3). Evaporation to dryness was carried out under the vacuum, and the powder of the specified substance of thin yellow was obtained (4.93g, 64% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) JIPIRIDO [3, 2-c:2', 3'-e] pyridazine (3)

3, 3'-dinitro -2, and the solution that dissolved $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (2.2g, 9.2mmol) for 2'-bipyridyl (2), and (0.25g, 1.0mmol) into water (7.2cm³) were added, and it agitated at the room temperature for 4.5 hours. Chloroform (100cm³) extracted this solution twice, the extract was washed with water, and evaporation to dryness was dried and carried out. The residue of ***** was *****ed from ethanol and the ***** needle crystal of the specified substance was obtained (0.16g, 89% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-3) 3 and 8- a jib -- ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine (4)

JIPIRIDO [3, 2-c:2', 3'-e] pyridazine (3), (1.6g, 8.6mmol), dark HBr (70cm³), and Br_2 (41.4g, 259mmol) were agitated at 100 degrees C for 12 hours. After cooling and precipitate were carried out the ** exception to the room temperature, and it washed by water and ethanol. The silica gel column chromatography refined sediment (eluent ethyl acetate). The powder of the specified substance of thin yellow was obtained according to evaporation to dryness (2.7g, 92% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) High molecular compound P-2 : Pori (the JIPIRIDO [3, 2-c:2', 3'-e] pyridazine -3, 8-diyl), PDpyPd (8)

Screw (1, 5-cyclo-octadiene) nickel (0) and nickel (cod)₂ (0.86, 3.1mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.41g, 2.6mmol) and 1 and 5-cyclo-octadiene (1.45cm³, 11.8mmol) were added to this. after

[1 hour churning], 3, and 8- a jib -- ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine (4), and (0.41g, 1.21mmol) were added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDPyPd (0.154g, 70% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C52.23%, H4.19%, and N24.37% calculated-value:

(C₁₀H₄N₄2.8H₂O) n:C52.08%, H4.20%, and N24.30%IR (KBr law) -- JIPIRIDO [3, 2-c:2', 3'-e]

pyridazine (3) and 3, and 8- a jib -- it is shown in drawing 1 with ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine. Drawing 1 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

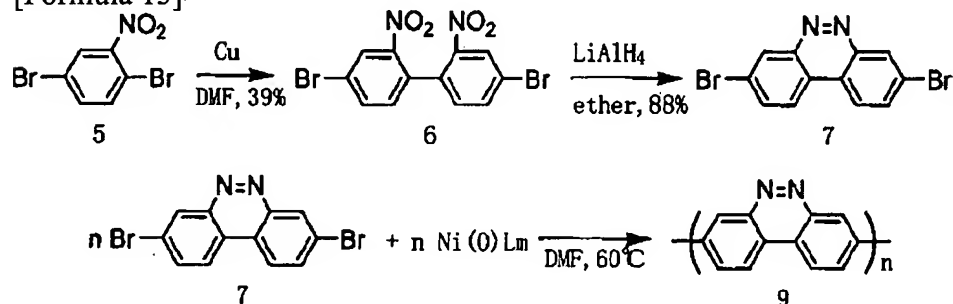
[0040] Mw of this high molecular compound P-2 (PDpyPd) was calculated from GPC analysis of a DMF dissolution part, it was 3.0x10³, and intrinsic viscosity eta was 0.10dLg⁻¹ (inside of 30 degrees C and a formic acid).

Example 2 (composition)

The reaction scheme of the synthetic high polymer P-1 of a high molecular compound P-1 (Pori (benzo [c] cinnoline -3, 8-diyl)) is shown below.

[0041]

[Formula 13]



[0042] 1) Synthetic 1-14 of a monomer, 4'-dibromo -2, a 2'-dinitro biphenyl (6)

A 1 in DMF (100cm³) and 4-dibromo-2-nitrobenzene (5), and (12g, 43mmol) were made to return with copper bronze (8.2g) for 4 hours. The reaction mixture was filtered and aqueous ammonia was added to the filtration object. Precipitate was carried out the ** exception and the silica gel column chromatography refined it (eluent CHCl₃/hexane = 1/1). Evaporation to dryness was carried out under the vacuum, and the powder of the specified substance of thin yellow was obtained (3.32g, 39% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) 3 and 8-dibromo benzo [c] cinnoline (7)

4 and 4-dibromo -2, a 2'-dinitro biphenyl (6), (1.2g, 3.0mmol), the dry ether (50cm³), and benzene (50cm³) were added to the dry ether (70cm³) and the mixture of LiAlH₄. It agitated at the room temperature for 2 hours, warmed with the water bath for 15 minutes, and cooled after that. Water was added, superfluous LiAlH₄ was decomposed, mixture was filtered, filtrate was evaporated, and separation purification of the residue was carried out under chloroform using the silica chromatography. The solvent was evaporated under the vacuum and the specified substance of thin yellow was obtained (0.88g, 88% of yield). It identified by elemental analysis, IR (KBr law), and ¹HNMR.

2) High molecular compound P-1 : Pori (benzo [c] cinnoline -3, 8-diyl), PBC (9)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)₂ (0.72, 2.6mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.34g, 2.2mmol) and 1 and 5-cyclo-octadiene (1.3cm³, 10.2mmol) were added to this. 3 and 8-dibromo benzo [c] cinnoline (7), and (0.35g, 1.0mmol) were added to the system of reaction after 1-

hour churning. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PBC (0.18g, about 100% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, since the thermal stability of this polymer is high, it is thought of that a difference is in an actual measurement and calculated value a little.

Actual measurement : C74.78%, H4.63%, and N13.79%, Br0.0% calculated-value:(C₁₂H₆N₂0.85H₂O) n:C74.49%, the result of H4.01% and N14.48%IR (KBr law) -- 1, a 4-dibromo-2-nitrobenzene (5), 4, and 4' - dibromo -2 and 2' -- it is shown in drawing 1 with - dinitro biphenyl (6) and 3, and 8-dibromo benzo [c] cinnoline (7). Drawing 1 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0043] Mw of this high molecular compound P-2 (PDpyPd) was calculated from GPC analysis of a DMF dissolution part, and was 1.64x10⁴.

Example 3 (measurement)

The result of having investigated the solubility (25 degrees C) over various solvents about the high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2 and P-1 (PBC) is shown in Table 1. It turned out that PDpyPd is dissolved in part to a polar organic solvent like DMF, dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), 1, and 3-dimethyl-2-imidazolidine (DMI), and good solubility is shown from Table 1 to an acidic solvent like a formic acid and a sulfuric acid. On the other hand, probably because PBC had few N numbers, it was inferior in solubility also to any of an organic solvent and an acidic solvent compared with PDpyPd. In addition, THF of front Naka is a tetrahydrofuran.

[0044]

[Table 1]

溶媒	PDpyPd	PBC
CF ₃ COOH	△	△△
H ₂ SO ₄	○	△
HCOOH	○	△
(CF ₃) ₂ CHOH	×	×
DMI	△△	△△
NMP	△△	△
DMF	△△	△△
DMSO	△△	△
THF	×	×
CHCl ₃	×	×

* ○ 可溶 △ 一部溶解 △△ やや溶解 × 不溶

[0045] Example 4 (measurement)

The spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured about the high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2, and P-1 (PBC).

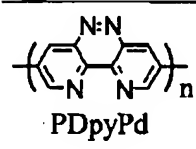
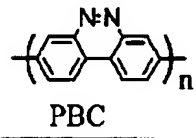
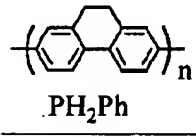
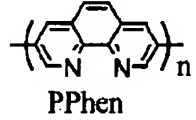
[0046] About PDpyPd, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 3 and Table 2. PL was measured in DMF, was shown in drawing 5 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing), and showed λ_{max} in Table 2.

[0047] About PBC, the visible ultraviolet absorption spectrum was measured in DMSO and HCOOH, and this result was shown in drawing 4 and Table 2. PL was measured in DMSO, was shown in drawing 6 about the excitation spectrum and the emission spectrum, and showed λ_{max} of luminescence in Table 2.

[0048] In addition, the data of Pori (1, the 10-phenanthroline -3, 8-Jill) and PPhen and the data of Pori (the dihydrophenanthroline -2, 7-diyl) and PH2Ph were written together to Table 2 for the comparison.

[0049]

[Table 2]

	UV-vis 吸収		PL		バンドギャップ/eV(計算値)	
	λ max(nm)	吸収端(nm)	λ max(nm)	UV	PL	
 PDpyPd	435	(DMF)	495	500	2.5	2.5
	370	(HCOOH)	460	500	2.7	2.5
 PBC	350	(DMSO)	415	447	3.0	2.8
	310,370	(HCOOH)	390	380,398	3.2	3.1~3.3
 PH ₂ Ph	361	(NMP)	—	—	—	—
 PPhen	382	(HCOOH)	410	413	3.0	3.0

[0050] If a visible ultraviolet absorption spectrum is considered, since an orthohydrogen exists in a biphenyl unit about PBC and PH₂Ph, it will be thought that steric hindrance exists and it will be thought that formation of pi-conjugated system which meets a polymer chain and spreads is checked. Since PDpyPd in a formic acid and PPhen are protonated, such a phenomenon is considered to be generated similarly. On the other hand, it was thought that, as for PDpyPd, such steric hindrance did not exist in DMSO and DMF, and the absorption peak has shifted to the long wavelength side in the fact and such an organic solvent.

[0051] About PL, PDpyPd has λ max of luminescence in a long wavelength side compared with PBC. Although the calculated band gap was shown in Table 2 from the absorption end and PL (λ max) of an absorption spectrum, respectively, it turns out that the band gap of PDpyPd is [/ else] small about 0.5eV.

[0052] Example 5 (measurement)

The high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2 and P-1 (PBC) are cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.1mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A result is shown in drawing 7. A trace speed is 50mVs-1, the inside a of drawing was 100mVs-1, a was performed by b and 2.3--2.1V (vs.Ag+/Ag) and c performed [b and c] scanning in 0--2.5V (vs.Ag+/Ag). In addition, as shown in a, change of the color of dark brown (dark brown) to brown (brown) was seen with potential change.

[0053] From drawing 7 c, a PBC film shows a reversible oxidation reduction cycle, a reduction peak (Epc) and an oxidation peak (Epa) are -2.02V and -1.82V (vs.Ag+/Ag), respectively, and these peaks support n-doping of PBC, and n-undoping. On the other hand, it turns out that a PDpyPd film has a peak corresponding to n-doping and n-undoping in 1.38V and 0.82V (vs.Ag+/Ag) by scanning of 0--2.5V (vs.Ag+/Ag). These results show that it originates in PDpyPd having imine nitrogen in a two-piece excess per repeat configuration compared with PPhen (referring to Epc of the after-mentioned table 3), and PBC, and is easier to be returned. On the other hand, in valve flow coefficient measured in -2.1-+2.3V about PDpyPd, although the reduction peak (-0.1V, -0.6V, -1.3Vvs.Ag+/Ag) of a three-stage was

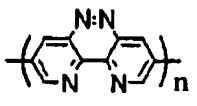
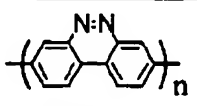
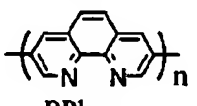
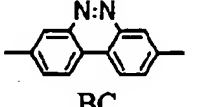
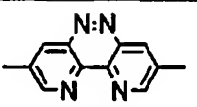
seen, coupling of the peak of -0.1V and -0.6V is carried out to the oxidation peak of 1.9V, and it turned out that it is what belongs to p-undoping peak of the p-dope PDpyPd of the 1.9V neighborhood.

[0054] valve flow coefficient data of DpyPd which are PDpyPd, PBC, PPhen and BC that is a monomer used as the raw material of PBC, and a monomer used as the raw material of PDpyPd also including the above data are gathered in Table 3. E10 is reduction potential.

[0055]

[Table 3]

(0 → -2.5 → 0V)

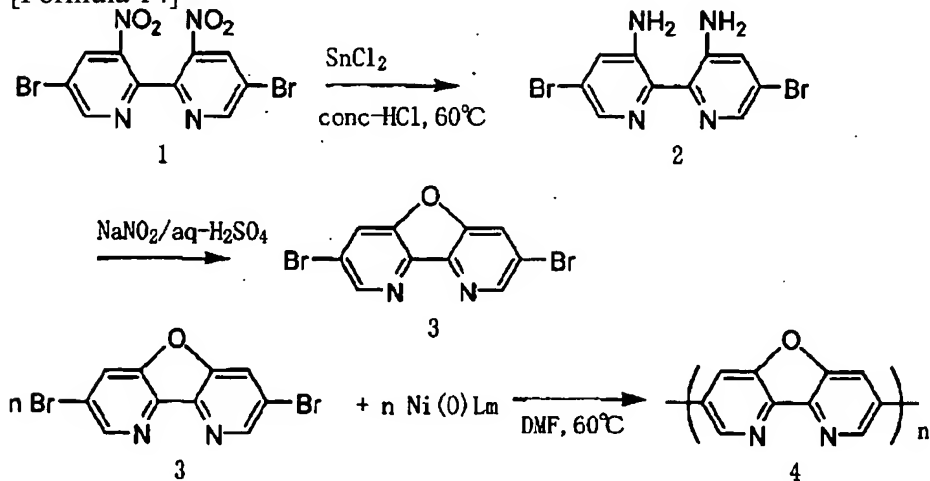
	酸化還元電位, V vs. Ag ⁺ /Ag (CH ₃ CN)		
	E _{pc}	E _{pa}	E ₁ ⁰
 PDpyPd	-1.38	-0.82	-1.10
 PBC	-2.02	-1.82	-1.92
 PPhen	-2.24	-1.98	-2.11
 BC	-1.96	-1.86	-1.91
 DpyPd	-1.64	-1.60	-1.62
	-2.34	-2.15	-2.25

[0056] Example 6 (composition)

The reaction scheme of the synthetic high polymer P-3 of a high molecular compound P-3 (Pori (the JIPRIDO [3, 2-b:2', 3'-d] furan -3, 7-diyl)) is shown below.

[0057]

[Formula 14]



[0058] 1) Synthetic 1-13 of a monomer, the 3'-diamino -5, 5'-dibromo -2, a 2'-bipyridine (2) 5 and 5-dibromo -3, 3'-dinitro -2, and 2'-bipyridine (1), and (4.60g, 11.4mmol) were added to the dark HCl (40cm³) solution of SnCl₂·2H₂O (24.5g, 106mmol), and was agitated at 60 degrees C for 2 hours. It cooled to the room temperature, and alkalinized in the NaOH water solution 20%, and chloroform extracted. The extract was rinsed and it dried by MgSO₄. The silica gel column chromatography (eluent chloroform) refined residue after solvent distilling off. The powder of the yellow specified substance was obtained after solvent distilling off (3.88g, 99% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) 3 and 7- a jib -- a ROMOJI pyrid [3, 2-b:2', 3'-d] furan (3)

3 and 3' -- the - diamino -5 and 5' - dibromo -2 and 2' - bipyridine (2), and (0.52g, 1.5mmol) were dissolved in the formic acid (2cm³) 80%, and NaNO₂ (0.15g, 12.2mmol) solution of concentrated sulfuric acid (1.5cm³) was dropped at this at 0-5 degrees C. This mixture was agitated at 50-60 degrees C, and was agitated for 10 minutes at 90 more degrees C after that until the gas evolution was lost. It alkalinized in the NaOH water solution 20%, chloroform extracted, and it dried by anhydrous [MgSO₄ / 4]. The silica gel column chromatography (eluent chloroform) refined residue after solvent distilling off. Distilling off of the solvent obtained the powder of the yellow specified substance (0.12g, 25% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) A high molecular compound P-3 (Pori (the JIPIRIDO [3, 2-b:2', 3'-d] furan -3, 7-diyl)), PDpyFu (4) Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)2 (0.25, 0.91mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.12g, 0.77mmol) and 1 and 5-cyclo-octadiene (0.43cm³, 350mmol) were added to this. after [10 minute churning], 3, and 7- a jib -- a ROMOJI pyrid [3, 2-b:2', 3'-d] furan (3), and (0.114g, 0.35mmol) were added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDTA, 2K⁺, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDpyFu (0.44g, 75% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C64.11%, H3.49%, and N15.14%, O14.20% calculated-value: (C₁₀H₄N₂O·0.95H₂O) n: C64.25%, H3.18%, and N14.99% and O16.69% IR (KBr law) -- 3 and 7- a jib -- it is shown in drawing 8 with a ROMOJI pyrid [3, 2-b:2', 3'-d] furan. Drawing 8 shows that the sharp peak of nu (C-Br) of the 1074cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0059] Mw of this high molecular compound P-3 (PDpyFu) was calculated from GPC analysis of a DMF dissolution part, and was 2.9x10³.

[0060] Example 7 (measurement)

About the high molecular compound P-3 (PDpyFu) obtained in the example 6, the solubility (25 degrees C) over various solvents was investigated. This result is shown in Table 4.

[0061]

[Table 4]

溶媒	PDpyFu
CF ₃ COOH	△
H ₂ SO ₄	○
HCOOH	○
DMI	×
NMP	△
DMF	△
DMSO	△
アセトン	×
CHCl ₃	×
MeOH	×

* ○ 可溶 △ 一部溶解 × 不溶

[0062] To a polar organic solvent like DMF, DMSO, and NMP, it dissolved in part, and it turned out to an acidic solvent like a formic acid and a sulfuric acid that PDpyFu is meltable.

[0063] Example 8 (measurement)

About the high molecular compound P-3 (PDpyFu) obtained in the example 6, the spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured.

[0064] About PDpyFu, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 9 and Table 5. PL was measured in DMF, was shown in drawing 10 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing), and showed λ_{max} in Table 5. In addition, in Table 5, it is written together for a comparison that the result of the visible ultraviolet absorption spectrum of Pori (a pyridine -2, 5-diyl) Ppy and Pori (2, the 2'-bipyridine -5, 5'-diyl) PBpy is DpyFu which is the monomer raw material of PDpyFu.

[0065]

[Table 5]

溶媒	PDpyFu	DpyFu	Ppy と PBpy
DMF	350	310	—
DMSO	350	—	—
NMP	355	—	—
HCOOH	410	330	370
H ₂ SO ₄	385	—	—
フィルム	395	—	—

[0066] As for λ_{max} of the visible ultraviolet absorption spectrum of PDpyFu, the direction of a formic acid has become the long wavelength side out of DMF. λ_{max} in a formic acid is in a long wavelength side rather than Ppy or PBpy. This is considered because pi-conjugated system spread by the condensation furan ring.

[0067] Moreover, by formation of pi-conjugated system, λ_{max} shifts to 40-80nm long wavelength side, and the PDpyFu consists of a monomer DpyFu which serves as a raw material of PDpyFu in DMF a long wavelength side rather than the inside of an organic solvent by the shape of a film.

[0068] About PL, PL peak in DMF is 400nm, and blue luminescence of a high quantum yield (absorbance 0.01) which results in 0.85 is obtained. PDpyFu in concentrated sulfuric acid shows the remarkable quantum yield (absorbance 0.05) of 0.42.

[0069] Example 9 (measurement)

The high molecular compound P-3 (PDpyFu) obtained in the example 6 is cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.10mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A trace speed is 100mVs⁻¹.

A result is shown in drawing 11 .

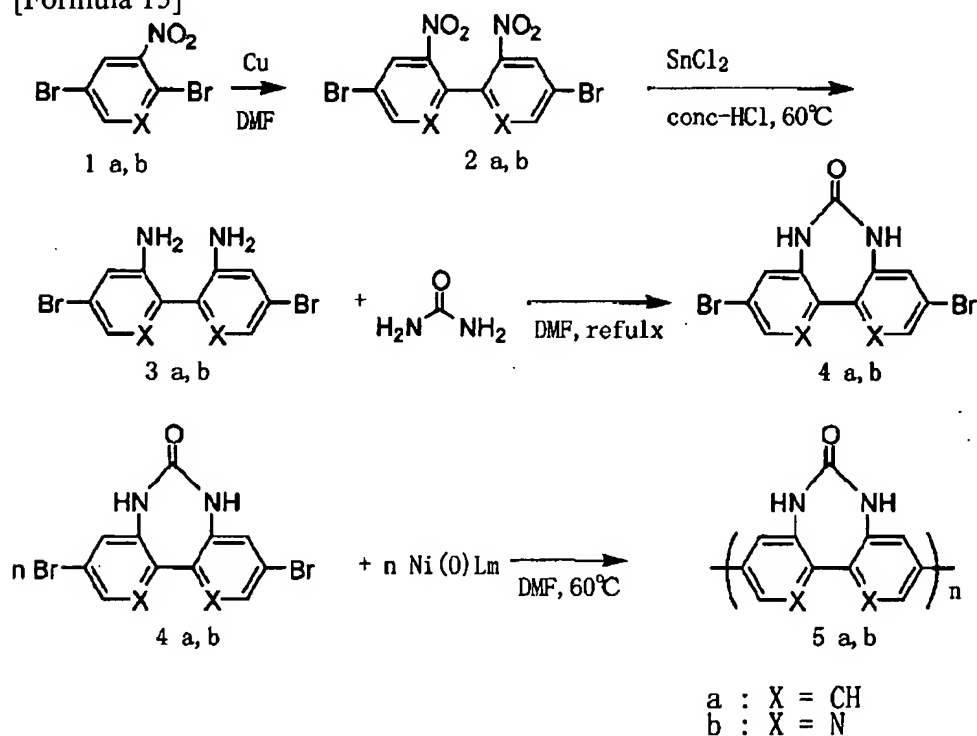
[0070] As shown in drawing 11 a, it has the oxidation reduction cycle which a PDpyFu film has a reduction peak in -1.5V and -2.2V, and has an oxidation peak in -2.0V and -1.8V (vs.Ag+/Ag). In addition, it considered as scanning of 0.0--2.4V. The reduction peak supports n-doping (doping level 0.4V and 0.2V) of PDpyFu, and n-undoping. Although the doping level of the 1st cycle is 0.6V, it is smaller 0.2-0.3v than the 2nd cycle. Moreover, although an oxidation peak exists in 1.3V and 1.6V in the oxidation field of 0.0-+2.0V as shown in drawing 11 a, it has disappeared in the 2nd cycle. In drawing 11 c, although +2.0--2.4V (vs.Ag+/Ag) are scanned, the 2nd n-doping peak and its undoping peak in -2.2V are small. On the other hand, 1st n-doping peak of -1.5V is divided into -1.9V and -1.6V, and it is thought that this is related to +0.5 and the large oxidation peak of +1.4V.

[0071] Example 10 (composition)

The reaction scheme of the synthetic high polymer P-4 of a high molecular compound P-4 (Pori (the dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON -3, 9-diyl)) is shown below. In addition, the thing of the high molecular compound P-5 of the following example 11 is also shown collectively.

[0072]

[Formula 15]



[0073] 1) Synthetic 1-14 of a monomer, 4'-dibromo -2, 2'-dinitrophenyl (2a)

It compounded like 1-1 of an example 2.

1-2) 2 and 2'-diamino-dibromo biphenyl (3a)

4, 4'-dibromo -2, and a 2'-dinitro biphenyl (2a) (2.8g, 7.0mmol) were added to the dark HCl (30cm³) solution of SnCl₂·2H₂O (15g, 6.5mmol). This mixture was agitated at 60 degrees C for 2 hours. After cooling to a room temperature, it alkalinized in the NaOH water solution 20%, and chloroform extracted mixture. The extract was rinsed and it dried by MgSO₄ (melting agent chloroform). The silica gel column chromatography refined residue after solvent distilling off. The powder of the specified substance of the yellow which blueness cut by solvent distilling off obtained (2.1g, 87% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-3) 3, 7-dibromo dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON (4a)

2, the 2'-diamino -4, and a 4'-dibromo biphenyl (3a) (0.51g, 1.5mmol) and a urea (0.30g, 5.0mmol) were added to DMF (15cm³), and it flowed back for 12 hours. This mixture was cooled and it diluted with

water (10cm³). When precipitate was filtered and rinsed and it dried under the vacuum, the powder of the white specified substance was obtained (0.52g, 95% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) High molecular compound P-4 : Pori (the dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON -3, 9-diyl), PDBDAz (5a)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)2 (g [0.93], 3.4mmol) were added during Desiccation DMF (40cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.47g, 3.0mmol) and 1 and 5-cyclo-octadiene (1.7cm³, 14mmol) were added to this. 3 and 9-dibromo dibenzo diazepine-6-ON (4a) (0.50g, 1.4mmol) was added to the system of reaction after churning for 10 minutes. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDT, 2K+, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDBDAz (0.26g, 91% of yield) of the specified substance was obtained. The result of elemental analysis is shown below.

Actual measurement: The result of N12.99% and O10.46%IR (KBr law) is shown in drawing 12 with 3 and 9-dibromo dibenzo diazepine-6-ON C72.58% and H4.97% N12.73%, O9.16% calculated-value: (C₁₃H₈N₂O.0.41H₂O) n:C72.42%, and H4.12%. Drawing 12 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0074] The curve of 2 molds of 4:6 was obtained from GPC analysis of a DMF dissolution part with the peak area, and Mw of this high molecular compound P-4 (PDBDAz) was calculated with 4.14x10³ and 2.66x10³ corresponding to this.

[0075] Example 11 (composition)

High molecular compound P-5: The synthetic reaction scheme of Pori (the JIPIRIDO [3, 2-d:2', 3'-f] diazepine-6-ON -3, 9-diyl) is as above-mentioned.

1) Synthetic 1-13 of a monomer, the 3'-diamino -5, 5'-dibromo -2, a 2'-bipyridine (3b)

It compounded like 1-1 of an example 6.

1-2) 3 and 9- a jib -- ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON (4b)

5, 5'-dibromo -3, the 3'-diamino -2, and a 2'-bipyridine (3b) (0.18g, 0.52mmol) and a urea (0.22g, 3.7mmol) were added to DMF (5cm³), and it flowed back for 12 hours. This mixture was cooled and it diluted with water (10cm³). When precipitate was filtered and rinsed and it dried under the vacuum, the powder of the specified substance of ***** was obtained (0.19g, 100% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) A high molecular compound P-2 (Pori (JIPIRIDO [3, 2-d:2', 3'-f] diazepine -3, 9-diyl)), PDpyDAz (5b)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)2 (0.28, 1.0mmol) were added during Desiccation DMF (15cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.14g, 0.9mmol) and 1 and 5-cyclo-octadiene (0.51cm³, 4.1mmol) were added to this. after [churning during 10 minutes], 3, and 9- a jib -- ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON (4b) (0.15g, 0.41mmol) was added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDTA, 2K+, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDPyDAz (0.025g, 30% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C56.42%, H3.95%, and N23.56%, O17.05% calculated-value: (C₁₁H₆N₄O.1.4H₂O) n:C56.12%, H3.77%, and N23.80% and O16.31%IR (KBr law) -- 3 and 9- a jib -- it is shown in drawing 13 with ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON. Drawing 13 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0076] Mw of this high molecular compound P-5 (PDpyDAz) was calculated from GPC analysis of a DMF dissolution part, and was 2.9×10^3 .

[0077] Example 12 (measurement)

The solubility (25 degrees C) over various solvents was investigated about the high molecular compound P-4 (PDBDAz) obtained in the examples 10 and 11, and P-5 (PDpyDAz). This result is shown in Table 6.

[0078]

[Table 6]

溶媒	PDBADz	PDpyADz
CF ₃ COOH	△	○
H ₂ SO ₄	△	○
HCOOH	△	○
DMI	△	○
NMP	△	○
DMF	△	○
DMSO	△	○
アセトン	×	×
CHCl ₃	×	×
MeOH	×	×

* ○ 可溶 △ 一部溶解 × 不溶

[0079] Although it is extent dissolved in part also to any of a polar organic solvent (DMF, DMSO, NMP, DMI) and an acidic solvent (a formic acid, sulfuric acid) so that clearly from Table 6, PDpyDAz originates in two imine nitrogen and shows good solubility also to any of a polar organic solvent and an acidic solvent.

[0080] Example 13 (measurement)

The spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured about the high molecular compound P-4 (PDBDAz) obtained in the examples 10 and 11, and P-5 (PDpyDAz).

[0081] About PDBDAz, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 14 and Table 7. PL was measured in DMF and shown in drawing 17 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing).

[0082] About PDpyDAz, the visible ultraviolet absorption spectrum was measured by the shape of the inside of DMSO and HCOOH, or a film (Film), and this result was shown in drawing 15 and Table 7. PL was measured in DMF and shown in drawing 18 about the excitation spectrum and the emission spectrum.

[0083] In addition, λ_{max} of the visible ultraviolet absorption spectrum of DBrDpyAz of a monomer used as the raw material of DBrDBDAz of the monomer used as the raw material of PDBDAz and PDpyDAz was written together to Table 7 for the comparison.

[0084]

[Table 7]

溶媒	(λ max(nm))			
	PDBDAz	PDpyDAz	DBrDBDAz	DBrDpyDAz
DMF	345	365	310	330
DMSO	—	365	—	—
NMP	355	—	—	—
HCOOH	320	430	305	390
フィルム	420	400	—	—

[0085] A visible ultraviolet absorption spectrum is described. By PDpyDAz, λ_{max} is [the direction in HCOOH] on the long wavelength side to λ_{max} being [the direction in HCOOH] on the short wavelength side out of DMF in PDBDAz. Such an inclination is the same also in each monomer. By PDpyDAz, since two imine nitrogen and urea units exist in a single system, as shown in drawing 16, in addition to the hydrogen bond same A type [the] as the inside of an organic solvent, the new intermolecular hydrogen bridge by hydrogenation of imine nitrogen generates this, and its smoothness of a polymer chain increases, and it is considered because pi-conjugated system is expanded in HCOOH. Therefore, it is larger than the formation of long wavelength by the difference in the corresponding solvent of a monomer. Moreover, with a high molecular compound without a urea unit, long wavelength-ization in HCCO is not seen like Pori (a pyridine -2, 5-diyl) or Pori (2, the 2'-bipyridine -5, 5'-diyl). Moreover, but [so] compared with an organic solvent, the formation of long wavelength does not have measurement with a film, either.

[0086] About PL, PL peak of 455nm and PDpyDAz of PL peak of PDBDAz was 480nm, and PDBDAz was [0.51 and PDpyDAz of the quantum yield] 0.34.

[0087] Example 14 (measurement)

The high molecular compound P-4 (PDBDAz) obtained in the examples 1 and 2 and P-5 (PDpyDAz) are cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.1mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A trace speed is 100mVs-1. A result is respectively shown in drawing 19 and 20.

[0088] First, as shown in drawing 19 a, when a PDBDAz film is made to scan in 0.0--2.0V (vs.Ag+/Ag), the reversible oxidation reduction cycle which has a reduction peak in -1.4V and has an oxidation peak in -1.1V is shown, and each peak corresponds to n-doping of PDBDAz, and n-undoping respectively. Although the doping level of the 1st cycle is 1.0V, in the 2nd cycle, it decreases to 0.5-0.6V.

[0089] As shown in drawing 19 b, in the oxidation side of 0V--1.5V, an oxidation peak exists in 0.4V and 1.2V, and, probably it is thought respectively that it is based on amine nitrogen and a PPP (poly para-phenylene) frame. Most of these peaks disappears from the 2nd cycle.

[0090] If it scans in +1.5--2.0V as shown in drawing 19 c, the reversible oxidation reduction peak corresponding to n-doping and n-undoping will be seen with the doping level of 0.5-0.6V of drawing 19 a and homotopic. However, the oxidation peak of 1.2V is still irreversible.

[0091] Moreover, as shown in drawing 20 a, when a PDpyDAz film is made to scan in 0.0--1.7V (vs.Ag+/Ag), the reversible oxidation reduction cycle which has a reduction peak in -1.4V and has an oxidation peak in -1.1V is shown, and each peak corresponds to n-doping of PDpyDAz, and n-undoping respectively. Although the doping level of the 1st cycle is 0.4V, in the 2nd cycle, it decreases to 0.2-0.3V.

[0092] As shown in drawing 20 b, in the oxidation side of 0V--1.0V, an oxidation peak exists in 0.4V and 1.2V, and, probably it is thought respectively that it is based on amine nitrogen and the poly pyridine frame. Most of these peaks disappears from the 2nd cycle.

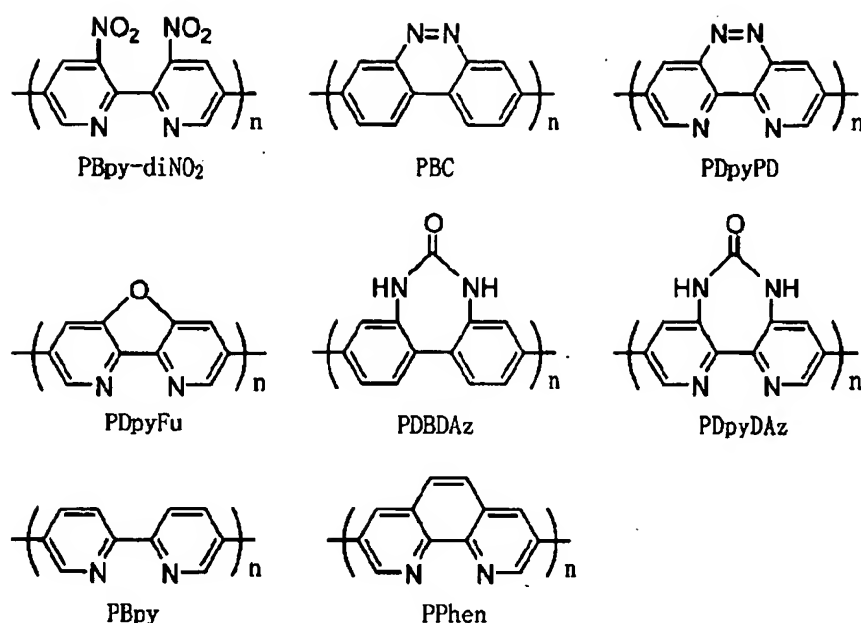
[0093] As shown in drawing 20 c, when it scanned in +1.0--1.7V, the oxidation peak according to the amino group to 0.4V and 0.1V and its doping peak of drawing 20 b and homotopic were seen. Respectively, the peak corresponding to n-doping and n-undoping has shifted in the forward direction so that the peak of -1.1V and +0.1V may be given.

[0094] Example 15 (oxidation reduction property)

The oxidation reduction properties of the following high molecular compounds also including the high molecular compound (polymer) compounded in the examples 1, 2, 6, 10, and 11 were compared.

[0095]

[Formula 16]



[0096] E10 (reduction potential) and Epc of the monomer used as the above-mentioned polymer and its raw material, and Epa(s) also including a thing as stated above are shown in Table 8. A polymer is a film-like as above-mentioned, and it asks for a monomer from cyclic voltammetry (valve flow coefficient) as a solution.

[0097]

[Table 8]

ポリマー	Epc	Epa	E ₁ ⁰	モノマー	Epc	Epa	E ₁ ⁰
PDpyPd	-1.38	-0.82	-1.10	DpyPd	-1.64	-0.60	-1.62
PDpyFu	-1.50	-1.00	-1.25	—	—	—	—
PDBDAz	-1.40	-1.10	-1.25	—	—	—	—
PDpyDAz	-1.40	-1.10	-1.25	—	—	—	—
PBpy-diNO ₂	-1.50	-1.30	-1.40	—	—	—	—
PBC	-2.02	-1.82	-1.92	BC	-1.96	-1.86	-1.91
PPhen	-2.24	-1.98	-2.11	Phen	—	—	-2.12 ^a
PBpy	-2.36	-2.00	-2.18	Bpy	—	—	-2.19 ^a
(-1.94) ^b							

^aV vs. Ag/AgCl (KCl 飽和溶液)

^bV vs. SCE (DMF)

[0098] The average of the potential of a reduction peak (n-doping) and an oxidation peak (n-undoping) is considered to be E10.

[0099] EA (electron affinity) of the repeat configuration unit (monomeric unit) which is the calculated value of the energy level of LUMO (lowest unoccupied molecular orbital) by MOPAC (parameter AM 1) is shown in Table 9. MOPAC count was performed using the CACHE system.

[0100]

[Table 9]

モノマー	EA/eV
Bpy	0.37
DBDAz	0.41
Phen	0.84
DpyDAz	0.88
DpyFu	0.93
BC	0.93
DpyPd	1.27
Bpy-diNO ₂	1.52

[0101] The relation of E10 of the polymer to EA of a monomeric unit is shown about three sorts of polymers similar to drawing 21. Drawing 21 shows that there is straight-line relation to E10 and EA ($E10 = \rho_1$ and $EA + a_1$, $\rho_1 = 2.37$, $a_1 = -4.11$ V).

[0102] The relation of E10 of the polymer to E10 of a monomeric unit is shown in drawing 22 about the same polymer as drawing 21. From drawing 22, it turns out that straight-line relation is shown, and the relation of $E10(\text{polymer}) = \rho_2$ and $E10(\text{monomer}) + a_2$, $\rho_2 = 2.07$, and $a_2 = 2.19$ V is shown. This result shows depending for reduction capacity on the electronic competence of a monomeric unit. However, by other polymers, probably in order to be based on the difference on structure, linearity was not shown.

[0103] Next, IP (ionization potential) of the polymer shown in Table 10 and a monomeric unit was calculated from measurement of UPS (UV spectroscopy). This value is shown in Table 10.

[0104]

[Table 10]

ポリマー	IP/eV		モノマー
PBpy	5.90	5.55	Bpy
PDpyFu	5.81	5.49	DpyFu
PDpyPd	5.61	5.38	DpyPd
PBC	5.40	5.35	BC
PBpy-diNO ₂	5.61	—	Bpy-diNO ₂

[0105] Although the relation of IP (IPM) to the monomeric unit of Polymer IP (IPP) was shown in drawing 23, it turns out that straight-line relation is shown ($IPP = \rho_3$ and $IPM + a_3$, $\rho_3 = 2.299$, $a_3 = -6.77$ V).

[0106] IP of the polymer of Table 10 corresponds to HOMO (highest occupied molecular orbital). On the other hand, the absorption end of a visible ultraviolet absorption spectrum and λ_{max} of photoluminescence support the band gap. The band structure of a polymer is acquired from the band gap calculated from the absorption end of HOMO energy level and a visible ultraviolet absorption spectrum. The band gap calculated from EA of a polymer, IP, and the absorption end is shown in Table 11.

Moreover, band structure is shown in drawing 24.

[0107]

[Table 11]

ポリマー	バンドギャップ ^a /eV(nm)	IP ^b /eV	EA ^c /eV
PBC	2.99(415)	5.40	2.41
PDpyPd	2.51(495)	5.61	3.10
PBpy-diNO ₂	2.53(490)	5.61	3.08
PDpyFu	3.10(400)	5.81	2.71
PDBDAz	3.22(385)	—	—
PDpyDAz	2.64(470)	—	—

a 吸収端 (可視紫外吸収スペクトル) からの計算値

b 測定値

c イオン化ポテンシャル-バンドギャップ

[0108]

[Effect of the Invention] According to this invention, pi conjugation high molecular compound with new electronic receptiveness is obtained. These can expect the application as macromolecule functional materials, such as an organic electroluminescence device and an organic FET device. Moreover, it can be used as electrochromic materials or an active material for cells.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new high molecular compound which has pi conjugated system which met the principal chain, the high molecular compound which can specifically expect the application as an ingredient for functional organic devices, such as an organic electroluminescence device and an organic FET (field-effect transistor) device, about the manufacture approach, and its manufacture approach. Moreover, it is related with the usage as electrochromic materials and an active material for cells.

[0002]

[Description of the Prior Art] In recent years, pi conjugation high molecular compound attracts attention as an electric and optical functional material, for example, is applied to the rechargeable battery, an organic electroluminescence device or an organic FET device, etc. For example, poly para-phenylene vinylene (PPV), poly para-phenylene (PPP), etc. are used for an organic electroluminescence device, and the poly aniline, the poly thiophene, etc. are used for the organic FET device for the poly thiophene etc. at the rechargeable battery. However, since many of ingredients developed so far are electron-donative giant molecules, the constraint of ** to which the design of a device is restricted has arisen. For example, it is a device deficient in the electronic transport capacity which most devices by which the current report is carried out become from an electron-donative ingredient in the field of a giant-molecule EL device, and an improvement of the further property is possible by combining with the polymeric materials from which it has electronic receptiveness and the property as an n mold conductor is expected. Moreover, although many reports of the p mold FET device of the electron-donative poly thiophene base are carried out in the field of the FET device using a conductive polymer, the FET device using an electronic receptiveness giant molecule is not yet reported, but an appearance of the polymeric materials which show n mold property with electronic receptiveness is desired.

[0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer [new pi conjugation high molecular compound which can expect the application as a functional material of functional organic devices, such as an organic electroluminescence device and an organic FET device, and which has electronic receptiveness, and] the manufacture approach. Moreover, it is offering the usage as electrochromic materials and an active material for cells.

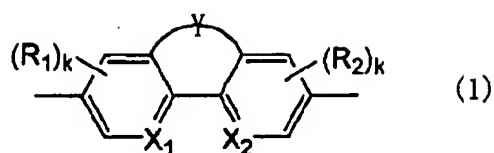
[0004]

[Means for Solving the Problem] Such a purpose is attained by following this invention.

[0005] (1) The high molecular compound which has the structure shown by the following formula (1) in a principal chain.

[0006]

[Formula 4]



[0007] In [type (1), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member.]

(2) The high molecular compound of the above (1) whose X1 and X2 in a formula (1) are nitrogen which constitutes a pyridine ring.

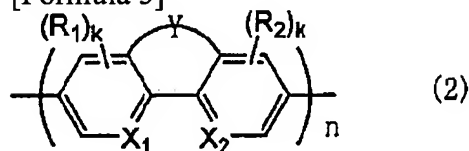
(3) The above (1) whose Y in a formula (1) is O, S, N=N, or R11 N-CO-NR12 (however, R11 and R12 may be the same respectively, or may differ from each other, and express hydrogen or a substituent.), or (2) high molecular compounds.

(4) One high molecular compound of above-mentioned (1) - (3) whose molecular weight is 1000 or more in weight average molecular weight.

(5) One high molecular compound of above-mentioned (1) - (4) shown by the formula (2).

[0008]

[Formula 5]

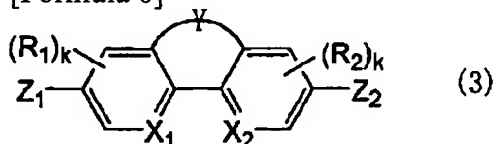


[0009] In [type (2), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. n expresses polymerization degree and is 5-1000.]

(6) The above (1) The manufacture approach of the high molecular compound obtained by carrying out dehalogenation of the dihalogen compound shown by the following formula (3) in one high molecular compound of - (5), and carrying out a polymerization.

[0010]

[Formula 6]



[0011] In [type (3), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member. Z1 and Z2 may be the same respectively, or they may differ from each other, and express a halogen.]

(7) The manufacture approach of the high molecular compound the above (6) that a dehalogenation polymerization is performed under existence of copper or a zero ** nickel compound.

(8) The above (1) Usage of the high molecular compound which uses one high molecular compound of - (5) as electrochromic materials or an active material for cells.

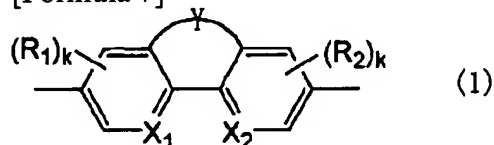
[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0013] The high molecular compound of this invention is a high molecular compound which has the structure shown by the following formula (1) in a principal chain, and is new pi conjugation high molecular compound which has electronic receptiveness.

[0014]

[Formula 7]



[0015] In a formula (1), X1 and X2 may be the same respectively, or they may differ from each other, and express the carbon which constitutes the benzene ring, or the nitrogen which constitutes a pyridine ring. R1 and R2 may be the same respectively, or they may differ from each other, and express a substituent. k is 0, 1, 2, or 3, when X1 and X2 constitute the benzene ring, and when a pyridine ring is constituted, it is 0, 1, or 2. Y expresses the atom or the atomic group for completing the heterocycle of 5 - 7 member.

[0016] When it explains further, X1 and X2 are the same, and when making electronic receptiveness discover, the combination of nitrogen is usually desirable [two] about a formula (1).

[0017] The substituents expressed with R1 and R2 may be any, for example, a nitro group, the amino group, etc. may be desirable and may be an alkyl group of carbon numbers 1-3 etc. As for k, it is desirable that it is 0 (namely, thing which does not have a substituent other than predetermined association) in any [of the benzene ring and a pyridine ring] case.

[0018] As the atom or the atomic group expressed with Y, preferably, O, S, N=N, R11 N-CO-NR12, etc. are mentioned, and O, N=N, R11 N-CO-NR12, etc. are desirable especially. Here, they may be the same respectively, or may differ and express hydrogen or a substituent (for example, alkyl group of carbon numbers 1-3), the usually same thing of R11 and R12 is desirable, and its combination of hydrogen is especially desirable.

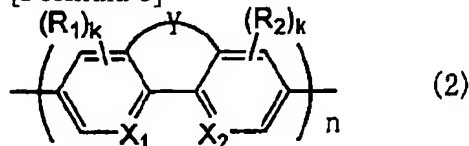
[0019] If the high molecular compound of this invention has the structure shown by the formula (1) in a principal chain, within limits which especially a limit does not have in the structure and do not check electronic receptiveness besides the configuration repeat unit of a formula (1) Although it has other configuration repeat units (for example, thing guided from a pyridine, a pyrimidine, a quinoline, a NAFUCHI lysine, etc.), it is desirable that it is the high molecular compound which consists of structure especially shown by the formula (1). In this case, although the configuration repeat unit of a formula (1) may be the same homopolymer and you may be the copolymer of the combination from which the configuration repeat unit of a formula (1) differs, it is desirable on a composite ease or a property that it is a homopolymer.

[0020] It is weight average molecular weight, as for the molecular weight of the high molecular compound of this invention, 1000 or more are desirable, and it is desirable to a pan that it is 3000-50000. It becomes easy to cast by having such molecular weight, and the reinforcement of mold goods improves by it.

[0021] As for especially the high molecular compound of this invention, what is shown by the following formula (2) is desirable, and its homopolymer is desirable especially.

[0022]

[Formula 8]

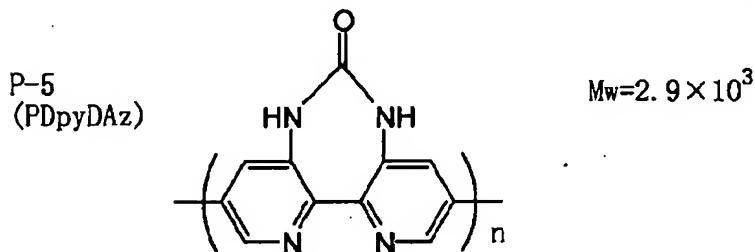
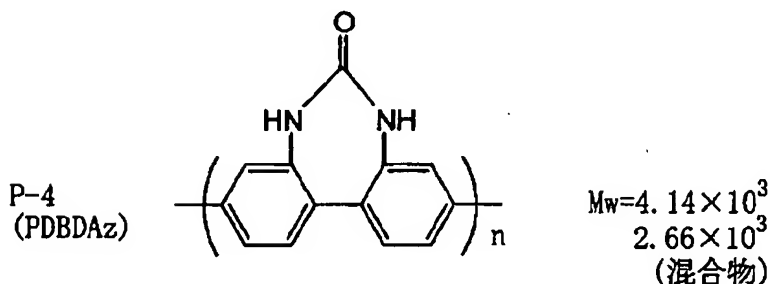
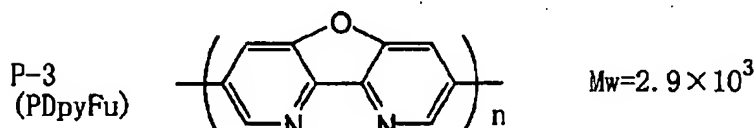
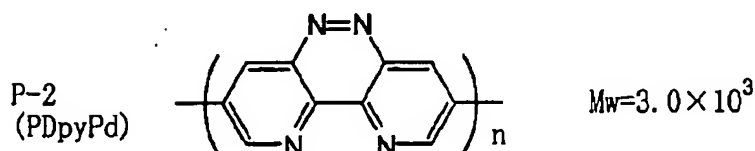
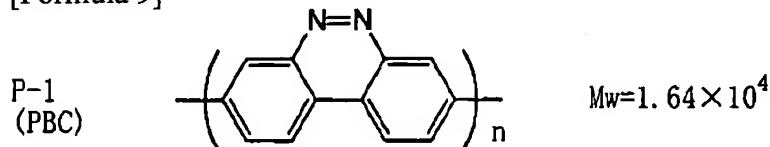


[0023] In a formula (2), X1, X2, R1, R2, k, and Y are a thing in a formula (1), and the thing of homonymy, and its same is said of a desirable thing. n is polymerization degree and is 5-1000.

[0024] Although the suitable example of the high molecular compound of this invention is shown below, it is not limited to these. It combines and weight average molecular weight Mw is shown. Moreover, all end groups are H.

[0025]

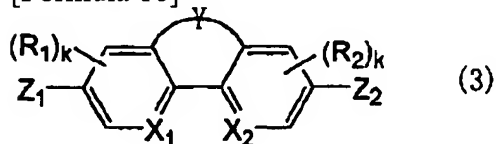
[Formula 9]



[0026] Such a high molecular compound is obtained by carrying out a polymerization while using as a start raw material the dihalogen compound shown by the following formula (3) according to the structure made into the purpose and carrying out dehalogenation of these.

[0027]

[Formula 10]



[0028] In a formula (3), X1, X2, R1, R2, k, and Y are a thing in a formula (1), and the thing of homonymy. Z1 and Z2 may be the same respectively, or they may differ from each other, and express a

halogen. Cl, Br, I, etc. are mentioned as a halogen expressed with Z1 and Z2. The same thing of Z1 and Z2 is desirable, and its combination of Br(s) etc. is desirable.

[0029] The metal or metallic compounds which has dehalogenation ability is made to exist on the occasion of dehalogenation and a polymerization. Various things are mentioned as the metal used for this invention, or metallic compounds. First, as a metal, the metal which causes the C-C coupling reaction of a reducibility metal or an organic halogenide is desirable, for example, 14 group metals, such as 13 group metals, such as 12 group metals, such as transition metals, such as 2 group metals, such as 1 group metals, such as Li, Na, and K, and Mg, calcium, and Ti, V, Cr, Fe, Co, nickel, Cu, and Zn, and aluminum, Ga, and Sn, are mentioned. the catalyst which consists of other metals or metallic compounds may be used for these metals if needed (the example which makes a nickel compound a catalyst in the similar polymerization using Mg -- a magazine "a macromolecule" -- indicated by the formula (1) in the 46th volume and 68 pages (1997)). Moreover, as metallic compounds, although there is especially no limit, the thing which makes the C-C coupling reaction of reducibility metallic compounds or an organic halogenide cause is desirable, for example, a zero ** nickel compound, a zero ** palladium compound, etc. are mentioned. When using these zero *****, such zero ***** itself may be used, and a divalent nickel compound, a divalent palladium compound, etc. may be added, and you may make it generate using reducing agents, such as Zinc Zn and a hydrazine, in the system of reaction. As a format of homopolymerization accompanied by C-C joint generation, polymerization formation of a publication can be mentioned [Japanese Patent Application No. / No. 42428 / six to] using a zero ** nickel compound.

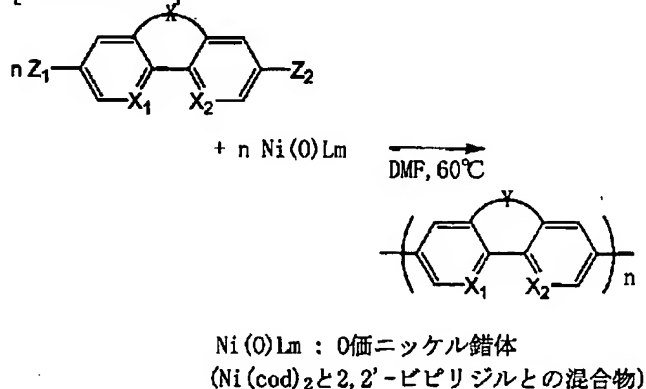
[0030] Copper or a zero ** nickel compound is desirable, and use of a zero ** nickel complex (for example, screw (1, 5-cyclo-octadiene) nickel:nickel2 (cod)) is desirable especially also in such.

[0031] Moreover, what is necessary is just to perform such a reaction at the temperature of about 60 degrees C using organic solvents, such as dimethylformamide (DMF), etc.

[0032] The reaction scheme in the case of obtaining the high molecular compound (however, k= 0) of a formula (2) is shown below.

[0033]

[Formula 11]



[0034] Thus, the high molecular compound obtained can be identified with elemental analysis, an infrared absorption spectrum (IR), etc. moreover, molecular weight -- a gel permeation chromatograph (GPC) -- it asks by law.

[0035] The high molecular compound of this invention is an electronic receptiveness compound, and the application with electronic receptiveness, such as an organic electroluminescence device and an organic FET device, as polymeric materials is expected. Moreover, the thing of X1=X2=N can also expect the application as a macromolecule chelating agent to a metal among the high molecular compounds of this invention.

[0036] Moreover, since the electrochemical reduction reaction accompanied by change of a color is shown, the high molecular compound of this invention can be used as electrochromic materials.

Moreover, it can also be used as an active material for cells using a oxidation reduction function. About

these concrete application approaches and gestalten, it applies to a well-known thing correspondingly.
[0037]

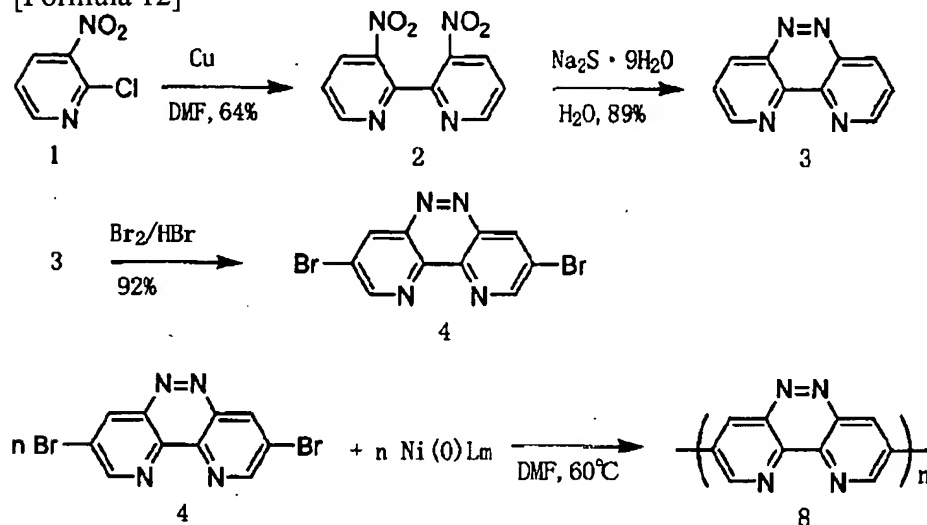
[Example] Hereafter, an example explains this invention concretely.

Example 1 (composition)

The reaction scheme of the synthetic high polymer P-2 of a high molecular compound P-2 (Pori (the JIPIRIDO [3, 2-c:2', 3'-e] pyridazine -3, 8-diyl)) is shown below.

[0038]

[Formula 12]



[0039] 1) Synthetic 1-13 of a monomer, 3-dinitro -2, a 2'-bipyridyl (2)

A 2-chloro-3-nitropyridine (1), (10g, 63.1mmol), N.N-dimethylformamide (30cm³), and the end (12g) of copper bronze powder were agitated all over the oil bath at 100 degrees C for 2 hours. The reaction mixture was filtered and aqueous ammonia was added to the filtration object. Precipitate was carried out the ** exception and the silica gel column chromatography refined it (eluent CHCl_3). Evaporation to dryness was carried out under the vacuum, and the powder of the specified substance of thin yellow was obtained (4.93g, 64% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) JIPIRIDO [3, 2-c:2', 3'-e] pyridazine (3)

3, 3'-dinitro -2, and the solution that dissolved $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (2.2g, 9.2mmol) for 2'-bipyridyl (2), and (0.25g, 1.0mmol) into water (7.2cm³) were added, and it agitated at the room temperature for 4.5 hours. Chloroform (100cm³) extracted this solution twice, the extract was washed with water, and evaporation to dryness was dried and carried out. The residue of ***** was *****ed from ethanol and the ***** needle crystal of the specified substance was obtained (0.16g, 89% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-3) 3 and 8- a jib -- ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine (4)

JIPIRIDO [3, 2-c:2', 3'-e] pyridazine (3), (1.6g, 8.6mmol), dark HBr (70cm³), and Br_2 (41.4g, 259mmol) were agitated at 100 degrees C for 12 hours. After cooling and precipitate were carried out the ** exception to the room temperature, and it washed by water and ethanol. The silica gel column chromatography refined sediment (eluent ethyl acetate). The powder of the specified substance of thin yellow was obtained according to evaporation to dryness (2.7g, 92% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) High molecular compound P-2 : Pori (the JIPIRIDO [3, 2-c:2', 3'-e] pyridazine -3, 8-diyl), PDpyPd (8)

Screw (1, 5-cyclo-octadiene) nickel (0) and nickel (cod)₂ (0.86, 3.1mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.41g, 2.6mmol) and 1 and 5-cyclo-octadiene (1.45cm³, 11.8mmol) were added to this. after

[1 hour churning], 3, and 8- a jib -- ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine (4), and (0.41g, 1.21mmol) were added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDPyPd (0.154g, 70% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C52.23%, H4.19%, and N24.37% calculated-value:

(C₁₀H₄N₄·2.8H₂O) n: C52.08%, H4.20%, and N24.30% IR (KBr law) -- JPIRIDO [3, 2-c:2', 3'-e]

pyridazine (3) and 3, and 8- a jib -- it is shown in drawing 1 with ROMOJI pyrid [3, 2-c:2', 3'-e] pyridazine. Drawing 1 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

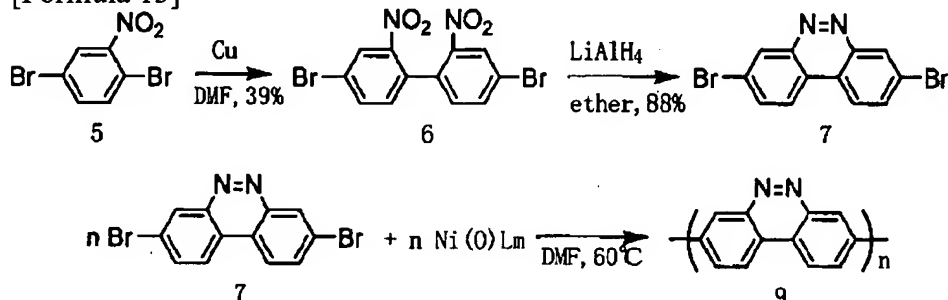
[0040] Mw of this high molecular compound P-2 (PDpyPd) was calculated from GPC analysis of a DMF dissolution part, it was 3.0x10³, and intrinsic viscosity eta was 0.10dLg⁻¹ (inside of 30 degrees C and a formic acid).

Example 2 (composition)

The reaction scheme of the synthetic high polymer P-1 of a high molecular compound P-1 (Pori (benzo [c] cinnoline -3, 8-diyl)) is shown below.

[0041]

[Formula 13]



[0042] 1) Synthetic 1-14 of a monomer, 4'-dibromo -2, a 2'-dinitro biphenyl (6)

A 1 in DMF (100cm³) and 4-dibromo-2-nitrobenzene (5), and (12g, 43mmol) were made to return with copper bronze (8.2g) for 4 hours. The reaction mixture was filtered and aqueous ammonia was added to the filtration object. Precipitate was carried out the ** exception and the silica gel column chromatography refined it (eluent CHCl₃/hexane = 1/1). Evaporation to dryness was carried out under the vacuum, and the powder of the specified substance of thin yellow was obtained (3.32g, 39% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) 3 and 8-dibromo benzo [c] cinnoline (7)

4 and 4-dibromo -2, a 2'-dinitro biphenyl (6), (1.2g, 3.0mmol), the dry ether (50cm³), and benzene (50cm³) were added to the dry ether (70cm³) and the mixture of LiAlH₄. It agitated at the room temperature for 2 hours, warmed with the water bath for 15 minutes, and cooled after that. Water was added, superfluous LiAlH₄ was decomposed, mixture was filtered, filtrate was evaporated, and separation purification of the residue was carried out under chloroform using the silica chromatography. The solvent was evaporated under the vacuum and the specified substance of thin yellow was obtained (0.88g, 88% of yield). It identified by elemental analysis, IR (KBr law), and ¹HNMR.

2) High molecular compound P-1 : Pori (benzo [c] cinnoline -3, 8-diyl), PBC (9)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)₂ (0.72, 2.6mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.34g, 2.2mmol) and 1 and 5-cyclo-octadiene (1.3cm³, 10.2mmol) were added to this. 3 and 8-dibromo benzo [c] cinnoline (7), and (0.35g, 1.0mmol) were added to the system of reaction after 1-

hour churning. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PBC (0.18g, about 100% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, since the thermal stability of this polymer is high, it is thought of that a difference is in an actual measurement and calculated value a little.

Actual measurement : C74.78%, H4.63%, and N13.79%, Br0.0% calculated-value:(C₁₂H₆N₂0.85H₂O) n:C74.49%, the result of H4.01% and N14.48%IR (KBr law) -- 1, a 4-dibromo-2-nitrobenzene (5), 4, and 4' - dibromo -2 and 2' -- it is shown in drawing 1 with - dinitro biphenyl (6) and 3, and 8-dibromo benzo [c] cinnoline (7). Drawing 1 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0043] Mw of this high molecular compound P-2 (PDpyPd) was calculated from GPC analysis of a DMF dissolution part, and was 1.64x10⁴.

Example 3 (measurement)

The result of having investigated the solubility (25 degrees C) over various solvents about the high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2 and P-1 (PBC) is shown in Table 1. It turned out that PDpyPd is dissolved in part to a polar organic solvent like DMF, dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), 1, and 3-dimethyl-2-imidazolidine (DMI), and good solubility is shown from Table 1 to an acidic solvent like a formic acid and a sulfuric acid. On the other hand, probably because PBC had few N numbers, it was inferior in solubility also to any of an organic solvent and an acidic solvent compared with PDpyPd. In addition, THF of front Naka is a tetrahydrofuran.

[0044]

[Table 1]

溶媒	PDpyPd	PBC
CF ₃ COOH	△	△△
H ₂ SO ₄	○	△
HCOOH	○	△
(CF ₃) ₂ CHOH	×	×
DMI	△△	△△
NMP	△△	△
DMF	△△	△△
DMSO	△△	△
THF	×	×
CHCl ₃	×	×

* ○ 可溶 △ 一部溶解 △△ やや溶解 × 不溶

[0045] Example 4 (measurement)

The spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured about the high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2, and P-1 (PBC).

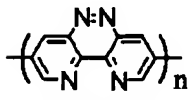
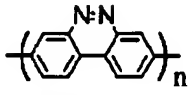
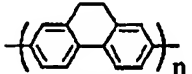
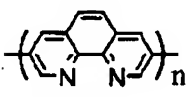
[0046] About PDpyPd, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 3 and Table 2. PL was measured in DMF, was shown in drawing 5 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing), and showed lambda_{max} in Table 2.

[0047] About PBC, the visible ultraviolet absorption spectrum was measured in DMSO and HCOOH, and this result was shown in drawing 4 and Table 2. PL was measured in DMSO, was shown in drawing 6 about the excitation spectrum and the emission spectrum, and showed lambda_{max} of luminescence in Table 2.

[0048] In addition, the data of Pori (1, the 10-phenanthroline -3, 8-Jill) and PPhen and the data of Pori (the dihydrophenanthroline -2, 7-diyl) and PH2Ph were written together to Table 2 for the comparison.

[0049]

[Table 2]

	UV-vis 吸収		PL		バンドギャップ/eV(計算値)	
	$\lambda_{\max}(\text{nm})$	吸収端(nm)	$\lambda_{\max}(\text{nm})$	UV	PL	
 PDpyPd	435	(DMF)	495	500	2.5	2.5
	370	(HCOOH)	460	500	2.7	2.5
 PBC	350	(DMSO)	415	447	3.0	2.8
	310,370	(HCOOH)	390	380,398	3.2	3.1~3.3
 PH ₂ Ph	361	(NMP)	—	—	—	—
 PPhen	382	(HCOOH)	410	413	3.0	3.0

[0050] If a visible ultraviolet absorption spectrum is considered, since an orthohydrogen exists in a biphenyl unit about PBC and PH₂Ph, it will be thought that steric hindrance exists and it will be thought that formation of pi-conjugated system which meets a polymer chain and spreads is checked. Since PDpyPd in a formic acid and PPhen are protonated, such a phenomenon is considered to be generated similarly. On the other hand, it was thought that, as for PDpyPd, such steric hindrance did not exist in DMSO and DMF, and the absorption peak has shifted to the long wavelength side in the fact and such an organic solvent.

[0051] About PL, PDpyPd has λ_{\max} of luminescence in a long wavelength side compared with PBC. Although the calculated band gap was shown in Table 2 from the absorption end and PL (λ_{\max}) of an absorption spectrum, respectively, it turns out that the band gap of PDpyPd is [/ else] small about 0.5eV.

[0052] Example 5 (measurement)

The high molecular compound P-2 (PDpyPd) obtained in the examples 1 and 2 and P-1 (PBC) are cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.1mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A result is shown in drawing 7. A trace speed is 50mVs-1, the inside a of drawing was 100mVs-1, a was performed by b and 2.3--2.1V (vs.Ag+/Ag) and c performed [b and c] scanning in 0--2.5V (vs.Ag+/Ag). In addition, as shown in a, change of the color of dark brown (dark brown) to brown (brown) was seen with potential change.

[0053] From drawing 7 c, a PBC film shows a reversible oxidation reduction cycle, a reduction peak (Epc) and an oxidation peak (Epa) are -2.02V and -1.82V (vs.Ag+/Ag), respectively, and these peaks support n-doping of PBC, and n-undoping. On the other hand, it turns out that a PDpyPd film has a peak corresponding to n-doping and n-undoping in 1.38V and 0.82V (vs.Ag+/Ag) by scanning of 0--2.5V (vs.Ag+/Ag). These results show that it originates in PDpyPd having imine nitrogen in a two-piece excess per repeat configuration compared with PPhen (referring to Epc of the after-mentioned table 3), and PBC, and is easier to be returned. On the other hand, in valve flow coefficient measured in -2.1-+2.3V about PDpyPd, although the reduction peak (-0.1V, -0.6V, -1.3Vvs.Ag+/Ag) of a three-stage was

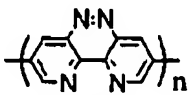
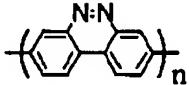
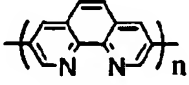
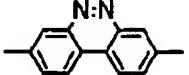
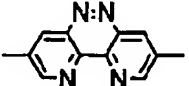
seen, coupling of the peak of -0.1V and -0.6V is carried out to the oxidation peak of 1.9V, and it turned out that it is what belongs to p-undoping peak of the p-dope PDpyPd of the 1.9V neighborhood.

[0054] valve flow coefficient data of DpyPd which are PDpyPd, PBC, PPhen and BC that is a monomer used as the raw material of PBC, and a monomer used as the raw material of PDpyPd also including the above data are gathered in Table 3. E10 is reduction potential.

[0055]

[Table 3]

(0 → -2.5 → 0V)

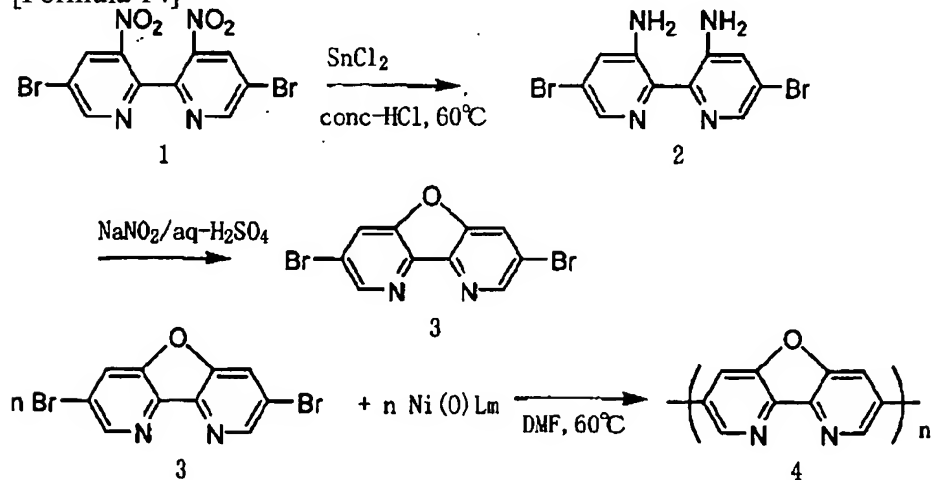
	酸化還元電位, V vs. Ag ⁺ /Ag (CH ₃ CN)		
	E _{pc}	E _{pa}	E ₁ ⁰
 PDpyPd	-1.38	-0.82	-1.10
 PBC	-2.02	-1.82	-1.92
 PPhen	-2.24	-1.98	-2.11
 BC	-1.96	-1.86	-1.91
 DpyPd	-1.64 -2.34	-1.60 -2.15	-1.62 -2.25

[0056] Example 6 (composition)

The reaction scheme of the synthetic high polymer P-3 of a high molecular compound P-3 (Pori (the JIPIRIDO [3, 2-b:2', 3'-d] furan -3, 7-diyl)) is shown below.

[0057]

[Formula 14]



[0058] 1) Synthetic 1-13 of a monomer, the 3'-diamino -5, 5'-dibromo -2, a 2'-bipyridine (2) 5 and 5-dibromo -3, 3'-dinitro -2, and 2'-bipyridine (1), and (4.60g, 11.4mmol) were added to the dark HCl (40cm³) solution of SnCl₂·2H₂O (24.5g, 106mmol), and was agitated at 60 degrees C for 2 hours. It cooled to the room temperature, and alkalinized in the NaOH water solution 20%, and chloroform extracted. The extract was rinsed and it dried by MgSO₄. The silica gel column chromatography (eluent chloroform) refined residue after solvent distilling off. The powder of the yellow specified substance was obtained after solvent distilling off (3.88g, 99% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-2) 3 and 7- a jib -- a ROMOJI pyrid [3, 2-b:2', 3'-d] furan (3)

3 and 3' -- the - diamino -5 and 5' - dibromo -2 and 2' - bipyridine (2), and (0.52g, 1.5mmol) were dissolved in the formic acid (2cm³) 80%, and NaNO₂ (0.15g, 12.2mmol) solution of concentrated sulfuric acid (1.5cm³) was dropped at this at 0-5 degrees C. This mixture was agitated at 50-60 degrees C, and was agitated for 10 minutes at 90 more degrees C after that until the gas evolution was lost. It alkalinized in the NaOH water solution 20%, chloroform extracted, and it dried by anhydrous [MgSO₄ / 4]. The silica gel column chromatography (eluent chloroform) refined residue after solvent distilling off. Distilling off of the solvent obtained the powder of the yellow specified substance (0.12g, 25% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) A high molecular compound P-3 (Pori (the JIPIRIDO [3, 2-b:2', 3'-d] furan -3, 7-diyl)), PDpyFu (4) Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)₂ (0.25, 0.91mmol) were added during Desiccation DMF (20cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.12g, 0.77mmol) and 1 and 5-cyclo-octadiene (0.43cm³, 350mmol) were added to this. after [10 minute churning], 3, and 7- a jib -- a ROMOJI pyrid [3, 2-b:2', 3'-d] furan (3), and (0.114g, 0.35mmol) were added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDTA, 2K⁺, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDpyFu (0.44g, 75% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C64.11%, H3.49%, and N15.14%, O14.20% calculated-value:

(C₁₀H₄N₂O·0.95H₂O) n:C64.25%, H3.18%, and N14.99% and O16.69%IR (KBr law) -- 3 and 7- a jib -- it is shown in drawing 8 with a ROMOJI pyrid [3, 2-b:2', 3'-d] furan. Drawing 8 shows that the sharp peak of nu (C-Br) of the 1074cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0059] Mw of this high molecular compound P-3 (PDpyFu) was calculated from GPC analysis of a DMF dissolution part, and was 2.9x10³.

[0060] Example 7 (measurement)

About the high molecular compound P-3 (PDpyFu) obtained in the example 6, the solubility (25 degrees C) over various solvents was investigated. This result is shown in Table 4.

[0061]

[Table 4]

溶媒	PDpyFu
CF ₃ COOH	△
H ₂ SO ₄	○
HCOOH	○
DMI	×
NMP	△
DMF	△
DMSO	△
アセトン	×
CHCl ₃	×
MeOH	×

* ○ 可溶 △ 一部溶解 × 不溶

[0062] To a polar organic solvent like DMF, DMSO, and NMP, it dissolved in part, and it turned out to an acidic solvent like a formic acid and a sulfuric acid that PDpyFu is meltable.

[0063] Example 8 (measurement)

About the high molecular compound P-3 (PDpyFu) obtained in the example 6, the spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured.

[0064] About PDpyFu, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 9 and Table 5. PL was measured in DMF, was shown in drawing 10 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing), and showed λ_{max} in Table 5. In addition, in Table 5, it is written together for a comparison that the result of the visible ultraviolet absorption spectrum of Pori (a pyridine -2, 5-diyl) Ppy and Pori (2, the 2'-bipyridine -5, 5'-diyl) PBpy is DpyFu which is the monomer raw material of PDpyFu.

[0065]

[Table 5]

溶媒	PDpyFu	DpyFu	Ppy と PBpy
DMF	350	310	—
DMSO	350	—	—
NMP	355	—	—
HCOOH	410	330	370
H ₂ SO ₄	385	—	—
フィルム	395	—	—

[0066] As for λ_{max} of the visible ultraviolet absorption spectrum of PDpyFu, the direction of a formic acid has become the long wavelength side out of DMF. λ_{max} in a formic acid is in a long wavelength side rather than Ppy or PBpy. This is considered because pi-conjugated system spread by the condensation furan ring.

[0067] Moreover, by formation of pi-conjugated system, λ_{max} shifts to 40-80nm long wavelength side, and the PDpyFu consists of a monomer DpyFu which serves as a raw material of PDpyFu in DMF a long wavelength side rather than the inside of an organic solvent by the shape of a film.

[0068] About PL, PL peak in DMF is 400nm, and blue luminescence of a high quantum yield (absorbance 0.01) which results in 0.85 is obtained. PDpyFu in concentrated sulfuric acid shows the remarkable quantum yield (absorbance 0.05) of 0.42.

[0069] Example 9 (measurement)

The high molecular compound P-3 (PDpyFu) obtained in the example 6 is cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.10mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A trace speed is 100mVs⁻¹.

A result is shown in drawing 11 .

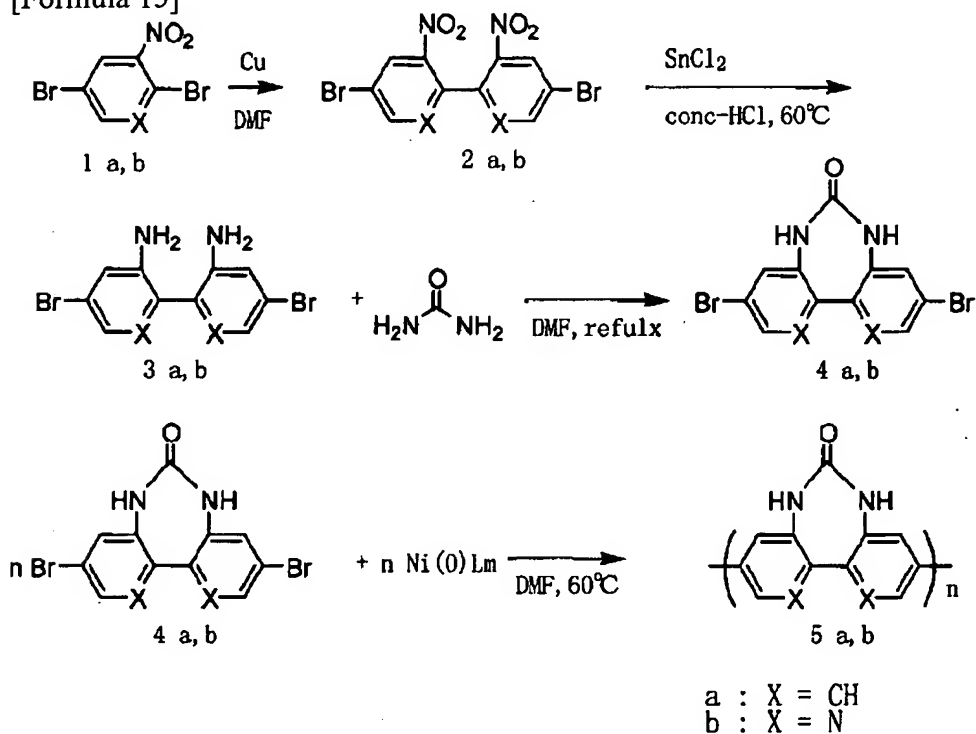
[0070] As shown in drawing 11 a, it has the oxidation reduction cycle which a PDpyFu film has a reduction peak in -1.5V and -2.2V, and has an oxidation peak in -2.0V and -1.8V (vs.Ag+/Ag). In addition, it considered as scanning of 0.0--2.4V. The reduction peak supports n-doping (doping level 0.4V and 0.2V) of PDpyFu, and n-undoping. Although the doping level of the 1st cycle is 0.6V, it is smaller 0.2-0.3v than the 2nd cycle. Moreover, although an oxidation peak exists in 1.3V and 1.6V in the oxidation field of 0.0--2.0V as shown in drawing 11 a, it has disappeared in the 2nd cycle. In drawing 11 c, although +2.0--2.4V (vs.Ag+/Ag) are scanned, the 2nd n-doping peak and its undoping peak in -2.2V are small. On the other hand, 1st n-doping peak of -1.5V is divided into -1.9V and -1.6V, and it is thought that this is related to +0.5 and the large oxidation peak of +1.4V.

[0071] Example 10 (composition)

The reaction scheme of the synthetic high polymer P-4 of a high molecular compound P-4 (Pori (the dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON -3, 9-diyl)) is shown below. In addition, the thing of the high molecular compound P-5 of the following example 11 is also shown collectively.

[0072]

[Formula 15]



[0073] 1) Synthetic 1-14 of a monomer, 4'-dibromo -2, 2'-dinitrophenyl (2a)

It compounded like 1-1 of an example 2.

1-2) 2 and 2'-diamino-dibromo biphenyl (3a)

4, 4'-dibromo -2, and a 2'-dinitro biphenyl (2a) (2.8g, 7.0mmol) were added to the dark HCl (30cm³) solution of SnCl₂·2H₂O (15g, 6.5mmol). This mixture was agitated at 60 degrees C for 2 hours. After cooling to a room temperature, it alkalinized in the NaOH water solution 20%, and chloroform extracted mixture. The extract was rinsed and it dried by MgSO₄ (melting agent chloroform). The silica gel column chromatography refined residue after solvent distilling off. The powder of the specified substance of the yellow which blueness cut by solvent distilling off obtained (2.1g, 87% of yield).

Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

1-3) 3, 7-dibromo dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON (4a)

2, the 2'-diamino -4, and a 4'-dibromo biphenyl (3a) (0.51g, 1.5mmol) and a urea (0.30g, 5.0mmol) were added to DMF (15cm³), and it flowed back for 12 hours. This mixture was cooled and it diluted with

water (10cm³). When precipitate was filtered and rinsed and it dried under the vacuum, the powder of the white specified substance was obtained (0.52g, 95% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) High molecular compound P-4 : Pori (the dibenzo [2, 1-d:1', 2'-f] diazepine-6-ON -3, 9-diyl), PDBDAz (5a)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)₂ (g [0.93], 3.4mmol) were added during Desiccation DMF (40cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.47g, 3.0mmol) and 1 and 5-cyclo-octadiene (1.7cm³, 14mmol) were added to this. 3 and 9-dibromo dibenzo diazepine-6-ON (4a) (0.50g, 1.4mmol) was added to the system of reaction after churning for 10 minutes. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDT, 2K+, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDBDAz (0.26g, 91% of yield) of the specified substance was obtained. The result of elemental analysis is shown below.

Actual measurement: The result of N12.99% and O10.46% IR (KBr law) is shown in drawing 12 with 3 and 9-dibromo dibenzo diazepine-6-ON C72.58% and H4.97% N12.73%, O9.16% calculated-value: (C₁₃H₈N₂O.0.41H₂O) n:C72.42%, and H4.12%. Drawing 12 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0074] The curve of 2 molds of 4:6 was obtained from GPC analysis of a DMF dissolution part with the peak area, and Mw of this high molecular compound P-4 (PDBDAz) was calculated with 4.14x10³ and 2.66x10³ corresponding to this.

[0075] Example 11 (composition)

High molecular compound P-5: The synthetic reaction scheme of Pori (the JIPIRIDO [3, 2-d:2', 3'-f] diazepine-6-ON -3, 9-diyl) is as above-mentioned.

1) Synthetic 1-13 of a monomer, the 3'-diamino -5, 5'-dibromo -2, a 2'-bipyridine (3b)

It compounded like 1-1 of an example 6.

1-2) 3 and 9- a jib -- ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON (4b)

5, 5'-dibromo -3, the 3'-diamino -2, and a 2'-bipyridine (3b) (0.18g, 0.52mmol) and a urea (0.22g, 3.7mmol) were added to DMF (5cm³), and it flowed back for 12 hours. This mixture was cooled and it diluted with water (10cm³). When precipitate was filtered and rinsed and it dried under the vacuum, the powder of the specified substance of ***** was obtained (0.19g, 100% of yield). Elemental analysis, IR (KBr law), and ¹HNMR performed identification.

2) A high molecular compound P-2 (Pori (JIPIRIDO [3, 2-d:2', 3'-f] diazepine -3, 9-diyl)), PDpyDAz (5b)

Screw (1, 5-cyclo OKITA diene) nickel (0) and nickel (cod)₂ (0.28, 1.0mmol) were added during Desiccation DMF (15cm³) at the room temperature, it considered as the solution and a 2 and 2'-bipyridyl (0.14g, 0.9mmol) and 1 and 5-cyclo-octadiene (0.51cm³, 4.1mmol) were added to this. after [churning during 10 minutes], 3, and 9- a jib -- ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON (4b) (0.15g, 0.41mmol) was added to the system of reaction. The mixture was made to react at 60-70 degrees C for 48 hours. To the room temperature, mixture was added to aqueous ammonia (500cm³) after cooling, and 1 evening churning was carried out. The powder carried out the ** exception was washed with a ** EDTA (EDTA, 2K+, and 2H₂O) water solution, warm water, rare aqueous ammonia, and a methanol, the vacuum drying was carried out at 100 degrees C for 15 hours, and PDPyDAz (0.025g, 30% of yield) of the specified substance was obtained. The result of elemental analysis is shown below. In addition, generally it is known that a 2 and 2'-bipyridine is a hydrate.

actual measurement: -- the result of C56.42%, H3.95%, and N23.56%, O17.05% calculated-value: (C₁₁H₆N₄O.1.4H₂O) n:C56.12%, H3.77%, and N23.80% and O16.31% IR (KBr law) -- 3 and 9- a jib -- it is shown in drawing 13 with ROMOJI pyrid [3, 2-d:2', 3'-f] diazepine-6-ON. Drawing 13 shows that the sharp peak of nu (C-Br) of the 1100-900cm⁻¹ neighborhood has disappeared by polymer-ization in a monomer.

[0076] Mw of this high molecular compound P-5 (PDpyDAz) was calculated from GPC analysis of a DMF dissolution part, and was 2.9x10³.

[0077] Example 12 (measurement)

The solubility (25 degrees C) over various solvents was investigated about the high molecular compound P-4 (PDBDAz) obtained in the examples 10 and 11, and P-5 (PDpyDAz). This result is shown in Table 6.

[0078]

[Table 6]

溶媒	PDBADz	PDpyADz
CF ₃ COOH	△	○
H ₂ SO ₄	△	○
HCOOH	△	○
DMI	△	○
NMP	△	○
DMF	△	○
DMSO	△	○
アセトン	×	×
CHCl ₃	×	×
MeOH	×	×

* ○ 可溶 △ 一部溶解 × 不溶

[0079] Although it is extent dissolved in part also to any of a polar organic solvent (DMF, DMSO, NMP, DMI) and an acidic solvent (a formic acid, sulfuric acid) so that clearly from Table 6, PDpyDAz originates in two imine nitrogen and shows good solubility also to any of a polar organic solvent and an acidic solvent.

[0080] Example 13 (measurement)

The spectrum of a visible ultraviolet absorption spectrum (UV-vis) and photoluminescence (PL) was measured about the high molecular compound P-4 (PDBDAz) obtained in the examples 10 and 11, and P-5 (PDpyDAz).

[0081] About PDBDAz, the visible ultraviolet absorption spectrum was measured in DMF and HCOOH, and this result was shown in drawing 14 and Table 7. PL was measured in DMF and shown in drawing 17 about the excitation spectrum (Excitation shows among drawing), and the emission spectrum (Emission shows among drawing).

[0082] About PDpyDAz, the visible ultraviolet absorption spectrum was measured by the shape of the inside of DMSO and HCOOH, or a film (Film), and this result was shown in drawing 15 and Table 7. PL was measured in DMF and shown in drawing 18 about the excitation spectrum and the emission spectrum.

[0083] In addition, λ_{max} of the visible ultraviolet absorption spectrum of DBrDpyAz of a monomer used as the raw material of DBrDBDAz of the monomer used as the raw material of PDBDAz and PDpyDAz was written together to Table 7 for the comparison.

[0084]

[Table 7]

(λ max(nm))				
溶媒	PDBDAz	PDpyDAz	DBrDBDAz	DBrDpyDAz
DMF	345	365	310	330
DMSO	—	365	—	—
NMP	355	—	—	—
HCOOH	320	430	305	390
フィルム	420	400	—	—

[0085] A visible ultraviolet absorption spectrum is described. By PDpyDAz, λ_{max} is [the direction in HCOOH] on the long wavelength side to λ_{max} being [the direction in HCOOH] on the short wavelength side out of DMF in PDBDAz. Such an inclination is the same also in each monomer. By PDpyDAz, since two imine nitrogen and urea units exist in a single system, as shown in drawing 16, in addition to the hydrogen bond same A type [the] as the inside of an organic solvent, the new intermolecular hydrogen bridge by hydrogenation of imine nitrogen generates this, and its smoothness of a polymer chain increases, and it is considered because pi-conjugated system is expanded in HCOOH. Therefore, it is larger than the formation of long wavelength by the difference in the corresponding solvent of a monomer. Moreover, with a high molecular compound without a urea unit, long wavelength-ization in HCCO is not seen like Pori (a pyridine -2, 5-diyl) or Pori (2, the 2'-bipyridine -5, 5'-diyl). Moreover, but [so] compared with an organic solvent, the formation of long wavelength does not have measurement with a film, either.

[0086] About PL, PL peak of 455nm and PDpyDAz of PL peak of PDBDAz was 480nm, and PDBDAz was [0.51 and PDpyDAz of the quantum yield] 0.34.

[0087] Example 14 (measurement)

The high molecular compound P-4 (PDBDAz) obtained in the examples 1 and 2 and P-5 (PDpyDAz) are cyclic. The voltammetry (valve flow coefficient) was measured. It carried out in the CH₃CN solution (0.1mol/L) of [NEt₄] and [BF₄], and the cast film on a platinum plate was made into the test portion. A trace speed is 100mVs-1. A result is respectively shown in drawing 19 and 20.

[0088] First, as shown in drawing 19 a, when a PDBDAz film is made to scan in 0.0--2.0V (vs.Ag+/Ag), the reversible oxidation reduction cycle which has a reduction peak in -1.4V and has an oxidation peak in -1.1V is shown, and each peak corresponds to n-doping of PDBDAz, and n-undoping respectively. Although the doping level of the 1st cycle is 1.0V, in the 2nd cycle, it decreases to 0.5-0.6V.

[0089] As shown in drawing 19 b, in the oxidation side of 0V--1.5V, an oxidation peak exists in 0.4V and 1.2V, and, probably it is thought respectively that it is based on amine nitrogen and a PPP (poly para-phenylene) frame. Most of these peaks disappears from the 2nd cycle.

[0090] If it scans in +1.5--2.0V as shown in drawing 19 c, the reversible oxidation reduction peak corresponding to n-doping and n-undoping will be seen with the doping level of 0.5-0.6V of drawing 19 a and homotopic. However, the oxidation peak of 1.2V is still irreversible.

[0091] Moreover, as shown in drawing 20 a, when a PDpyDAz film is made to scan in 0.0--1.7V (vs.Ag+/Ag), the reversible oxidation reduction cycle which has a reduction peak in -1.4V and has an oxidation peak in -1.1V is shown, and each peak corresponds to n-doping of PDpyDAz, and n-undoping respectively. Although the doping level of the 1st cycle is 0.4V, in the 2nd cycle, it decreases to 0.2-0.3V.

[0092] As shown in drawing 20 b, in the oxidation side of 0V--1.0V, an oxidation peak exists in 0.4V and 1.2V, and, probably it is thought respectively that it is based on amine nitrogen and the poly pyridine frame. Most of these peaks disappears from the 2nd cycle.

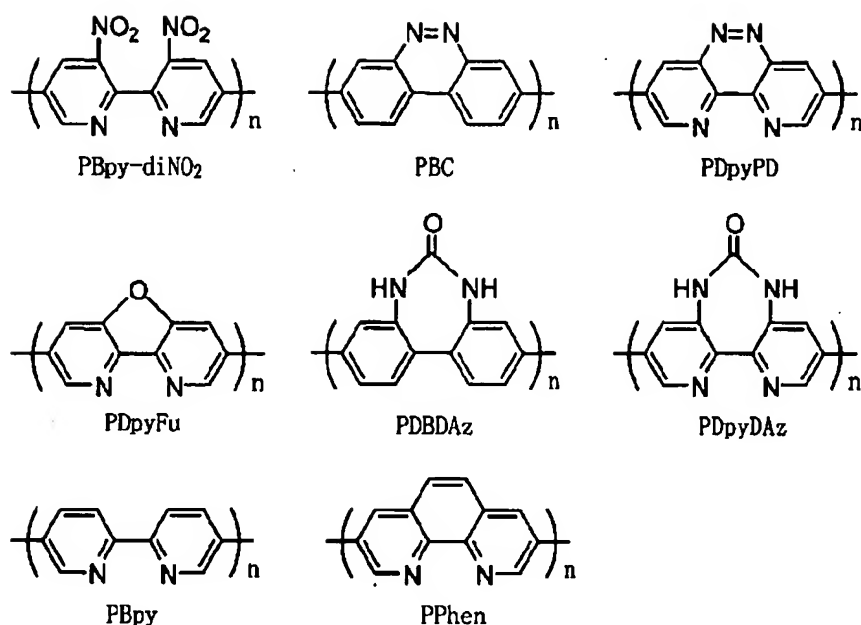
[0093] As shown in drawing 20 c, when it scanned in +1.0--1.7V, the oxidation peak according to the amino group to 0.4V and 0.1V and its doping peak of drawing 20 b and homotopic were seen. Respectively, the peak corresponding to n-doping and n-undoping has shifted in the forward direction so that the peak of -1.1V and +0.1V may be given.

[0094] Example 15 (oxidation reduction property)

The oxidation reduction properties of the following high molecular compounds also including the high molecular compound (polymer) compounded in the examples 1, 2, 6, 10, and 11 were compared.

[0095]

[Formula 16]



[0096] E10 (reduction potential) and Epc of the monomer used as the above-mentioned polymer and its raw material, and Epa(s) also including a thing as stated above are shown in Table 8. A polymer is a film-like as above-mentioned, and it asks for a monomer from cyclic voltammetry (valve flow coefficient) as a solution.

[0097]

[Table 8]

ポリマー	Epc	Epa	E ₁ ⁰	モノマー	Epc	Epa	E ₁ ⁰
PDpyPd	-1.38	-0.82	-1.10	DpyPd	-1.64	-0.60	-1.62
PDpyFu	-1.50	-1.00	-1.25	—	—	—	—
PDBDAz	-1.40	-1.10	-1.25	—	—	—	—
PDpyDAz	-1.40	-1.10	-1.25	—	—	—	—
PBpy-diNO ₂	-1.50	-1.30	-1.40	—	—	—	—
PBC	-2.02	-1.82	-1.92	BC	-1.96	-1.86	-1.91
PPhen	-2.24	-1.98	-2.11	Phen	—	—	-2.12 ^a
PBpy	-2.36	-2.00	-2.18	Bpy	—	—	-2.19 ^a
							(-1.94) ^b

^aV vs. Ag/AgCl (KCl 飽和溶液)

^bV vs. SCE (DMF)

[0098] The average of the potential of a reduction peak (n-doping) and an oxidation peak (n-undoping) is considered to be E10.

[0099] EA (electron affinity) of the repeat configuration unit (monomeric unit) which is the calculated value of the energy level of LUMO (lowest unoccupied molecular orbital) by MOPAC (parameter AM 1) is shown in Table 9. MOPAC count was performed using the CAChe system.

[0100]

[Table 9]

モノマー	EA/eV
Bpy	0.37
DBDAz	0.41
Phen	0.84
DpyDAz	0.88
DpyFu	0.93
BC	0.93
DpyPd	1.27
Bpy-diNO ₂	1.52

[0101] The relation of E10 of the polymer to EA of a monomeric unit is shown about three sorts of polymers similar to drawing 21. Drawing 21 shows that there is straight-line relation to E10 and EA ($E10 = \rho_1$ and $EA + a_1$, $\rho_1 = 2.37$, $a_1 = -4.11V$).

[0102] The relation of E10 of the polymer to E10 of a monomeric unit is shown in drawing 22 about the same polymer as drawing 21. From drawing 22, it turns out that straight-line relation is shown, and the relation of $E10(\text{polymer}) = \rho_2$ and $E10(\text{monomer}) + a_2$, $\rho_2 = 2.07$, and $a_2 = 2.19V$ is shown. This result shows depending for reduction capacity on the electronic competence of a monomeric unit. However, by other polymers, probably in order to be based on the difference on structure, linearity was not shown.

[0103] Next, IP (ionization potential) of the polymer shown in Table 10 and a monomeric unit was calculated from measurement of UPS (UV spectroscopy). This value is shown in Table 10.

[0104]

[Table 10]

ポリマー	IP/eV		モノマー
PBpy	5.90	5.55	Bpy
PDpyFu	5.81	5.49	DpyFu
PDpyPd	5.61	5.38	DpyPd
PBC	5.40	5.35	BC
PBpy-diNO ₂	5.61	—	Bpy-diNO ₂

[0105] Although the relation of IP (IPM) to the monomeric unit of Polymer IP (IPP) was shown in drawing 23, it turns out that straight-line relation is shown ($IPP = \rho_3$ and $IPM + a_3$, $\rho_3 = 2.299$, $a_3 = -6.77V$).

[0106] IP of the polymer of Table 10 corresponds to HOMO (highest occupied molecular orbital). On the other hand, the absorption end of a visible ultraviolet absorption spectrum and λ_{max} of photoluminescence support the band gap. The band structure of a polymer is acquired from the band gap calculated from the absorption end of HOMO energy level and a visible ultraviolet absorption spectrum. The band gap calculated from EA of a polymer, IP, and the absorption end is shown in Table 11. Moreover, band structure is shown in drawing 24.

[0107]

[Table 11]

ポリマー	バンドギャップ ^a /eV(nm)	IP ^b /eV	EA ^c /eV
PBC	2.99(415)	5.40	2.41
PDpyPd	2.51(495)	5.61	3.10
PBpy-diNO ₂	2.53(490)	5.61	3.08
PDpyFu	3.10(400)	5.81	2.71
PDBDAz	3.22(385)	—	—
PDpyDAz	2.64(470)	—	—

a 吸収端（可視紫外吸収スペクトル）からの計算値

b 測定値

c イオン化ポテンシャル-バンドギャップ

[0108]

[Effect of the Invention] According to this invention, pi conjugation high molecular compound with new electronic receptiveness is obtained. These can expect the application as macromolecule functional materials, such as an organic electroluminescence device and an organic FET device. Moreover, it can be used as electrochromic materials or an active material for cells.

[Translation done.]